538. *The Detoxication of Palladium Catalysts Poisoned by Various Metallic Ions.*

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The desorption of zinc-, cadmium-, lead-, mercury-, and arsenic-containing ions from the surface of palladium catalysts has been studied by various methods, the restoration of the activity of palladium catalysts for the hydrogenation of cyclohexene in ethyl alcohol at 20° being taken as a criterion. The catalysts were previously poisoned by these ions, in the form of their acetates, at various temperatures; and the various methods employed for the restoration of their activity were (i) washing with various liquids, (ii) treatment with an unsaturated organic substance, and (iii) treatment with an excess of an organic sulphide poison, in order to displace the metallic ions by mass action: this was followed by oxidation of the organic sulphide poison, in order to change it from an unshielded to a shielded form, in which state it becomes non-toxic and is easily removed by washing. It has been found that in some cases an almost complete, and in others a partial, restoration of the original activity of the catalyst was obtained, this being dependent on the temperature of the adsorption of these toxic cations and their projectional area. It was found that, with the increase in both of these factors, less reactivation of the catalyst was obtained.

MAXTED and MARSDEN [1] have studied the toxicities of various metallic ions, and have discussed them on the basis of their respective atomic radii. In a later paper, Maxted and Moon [2] dealt with the poisoning effects of various metallic ions from the standpoint of

[1] Maxted and Marsden, *J.*, 1940, 469.
[2] Maxted and Moon, *J.*, 1949, 2171.

their electronic structure. Maxted *et al.*[3] have found that the toxicities of various organic poisons vanish if they are changed from a non-shielded to a shielded structure by simple oxidation, that is by means of peracids in the presence of hydrogen peroxide, the activity of the catalyst being completely restored.

In this part of the work, small quantities of metallic ions were applied to unsupported palladium catalysts at 20°, 50°, 78°, and 105°, and to palladium supported on thoria at 150°. The relative restoration of the activity of palladium catalysts for the hydrogenation of cyclohexene was studied by various methods on separate samples of the catalysts. Those samples which regained their original activity by simpler methods, *e.g.*, by washing or by treatment with an unsaturated organic substance, were not examined by the more complicated method, namely, by treatment with an organic sulphide as the poison, followed by subsequent oxidation. Those samples which only partially regained their activity by the former methods were, however, dealt with by the latter method.

EXPERIMENTAL

The unsupported palladium was made by the reduction of palladium chloride by formaldehyde solution, then washed, and dried at 110°. The supported palladium was made by the usual method, as described in our earlier communication (*J.*, 1961, 4137) and dried at 200°. The ratio of the catalyst to the support was kept at 6 mg. of palladium to 2 g. of thoria, a stock of the catalyst being made, and fixed amounts being weighed out separately for each measurement.

0·025 g. of unsupported palladium was taken for all these measurements, the standard hydrogenation charge being the above weight of the catalyst, 1 c.c. of cyclohexene, 8·5 c.c. of alcohol, 0·5 c.c. of acetic acid, and 1 c.c. of water. The poisons were used as their acetates, except in the case of arsenic, which was made by dissolving a known quantity of arsenious oxide in water and adding 5 c.c. of acetic acid. The remaining poisons were dissolved directly in water and made up to the required volume in a graduated flask. 1 c.c. of the standard solutions contained, in each case, 5×10^{-5} mole of the metallic acetates or arsenious oxide. These poisons were applied in the concentration of 5×10^{-5} mole for unsupported palladium and 5×10^{-4} mole for supported palladium per batch.

Revival of Unsupported Palladium Poisoned by Zinc Acetate.—5×10^{-5} mole of zinc acetate was applied to 0·025 g. of palladium catalyst at 20°, 50°, 78°, and 105°, in four different reaction pipettes at each of these temperatures and in the presence of 5 c.c. of alcohol, the pipettes being kept for 15 hr. at the above temperatures. The catalysts treated at 20° were in liquid suspension, whereas those samples at other temperatures were dried after treatment for 15 hr.

The activity of 0·025 g. of the unsupported catalyst was determined by a blank run, the charge being that already given; the amount of hydrogen absorbed during the first 10 min. was taken as a measure of the activity.

The activities of the poisoned catalysts, previously treated at various temperatures, were measured for 10 min., it being found that, as the temperature of the adsorption of the poison was increased, the activity fell.

The second samples of the catalysts, treated at various temperatures, were washed twice with water, ethyl acetate, 2% (v/v in water) acetic acid, and ethyl alcohol, in turn. Then the activity was tested. The activity of the catalyst treated at 20° was completely restored, whereas catalysts treated at other temperatures regained only a part of their original activity.

The third samples of the catalysts, which had been treated at 50°, 78°, and 105°, were then treated with a mixture of 5 c.c. of cyclohexene and 5 c.c. of alcohol, then shaken for 30 min. and set aside for 15 hr. at room temperature. They were then washed with ethyl acetate and alcohol, after which their activity was tested. It was found that the samples which had been poisoned at 50° and 78° regained their activities almost completely, whereas that poisoned at 105° was only partially reactivated. The fourth sample of the catalyst previously poisoned at 105° was then treated with 3 c.c. of diethyl sulphide in 5 c.c. of alcohol, shaken for 30 min., and kept for 15 hr. This was subsequently washed with ethyl acetate and ethyl alcohol; then the catalyst was suspended in 10 c.c. of water, and 5×10^{-3} mole of permolybdic acid and 3 c.c. of 30% hydrogen peroxide were added. The reaction started slowly, but subsequently

[3] Maxted *et al.*, *J.*, 1945, 766; 1948, 1093; 1952, 4284.

became fast. When the reaction had ceased, a further charge of 3 c.c. of hydrogen peroxide was added and the process repeated three times. The mixture was then boiled, and the solid was collected in a centrifuge, washed several times with water, and twice with ethyl acetate followed by alcohol, after which the activity was tested. It was found that, even after this treatment, the catalyst poisoned at 105° did not regain its original activity. These measurements are summarised in Table 1.

TABLE 1.

Activity of 0·025 g. of palladium (unpoisoned)/10 min. = 132 c.c.

Zinc acetate = 5×10^{-5} mole throughout.

Treated at	20°	50°	78°	105°
Poisoned activity c.c. H_2/10 min.	27	21	20	12
Activity after washing	129	84	61	19
Activity after cyclohexene treatment	—	130	127	61
Activity after diethyl sulphide treatment, followed by oxidation...	—	—	—	108

The activity of the catalyst poisoned at 105°, and then treated with diethyl sulphide and washed, was also tested. It was found that this activity was very low, *e.g.*, only 3 c.c. of hydrogen were absorbed in 10 min., showing that the organic sulphide is not removed by washing, and that this poison is also adsorbed on other bare active sites, giving a low activity.

Cadmium Acetate.—The procedure described above was also employed in this case. The activity of the palladium catalyst, previously poisoned at 20°, could be completely restored by simple washing with 7% (v/v in water) acetic acid, while that of the samples previously poisoned at 50°, 78°, and 105° was only partially restored. A partial restoration of the activity was also obtained by treatment with cyclohexene. The catalyst samples poisoned at 50° and

TABLE 2.

Cadmium acetate = 5×10^{-5} mole throughout.

Treated at	20°	50°	78°	105°
Poisoned activity c.c. H_2/10 min.	19	14	14	8
Activity after washing	124	63	49	35
Activity after cyclohexene treatment	—	89	74	55
Activity after diethyl sulphide treatment, followed by oxidation...	—	123	121	94

78° regained most of their activity on treatment with diethyl sulphide and subsequent oxidation, while that poisoned at 105° was not restored to its original activity by any of these methods. These results are summarised in Table 2.

Lead Acetate.—The procedure described above was used. The activity of the catalyst, previously poisoned at 20°, was not restored by simple washing, but it was regained almost completely on treatment with cyclohexene: further, samples poisoned at 50° and 78° regained most of their activity after treatment with diethyl sulphide and subsequent oxidation, whereas that poisoned at 105° was only partially reactivated. These results are summarised in Table 3.

TABLE 3.

Lead acetate = 5×10^{-5} mole throughout.

Treated at	20°	50°	78°	105°
Poisoned activity c.c. H_2/10 min.	9	9	8	5
Activity after washing	72	34	23	10
Activity after cyclohexene treatment	126	69	54	38
Activity after diethyl sulphide treatment and subsequent oxidation	—	120	114	81

The Figure shows the stepwise detoxication of palladium catalyst poisoned by lead acetate at 50°.
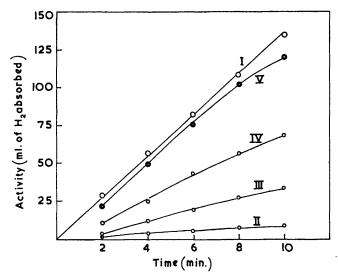
Mercuric Acetate.—The toxicity of this poison was found to be similar to that of lead acetate. Palladium previously poisoned at 20° was found to regain most of its activity on treatment with cyclohexene, whereas that poisoned at 50° and 78° regained its activity only on treatment with diethyl sulphide and subsequent oxidation. Palladium poisoned at 105° regained only a part of its original activity, even after the latter treatment. The results are summarised in Table 4.

TABLE 4.

Mercuric acetate $= 5 \times 10^{-5}$ mole throughout.

Treated at	20°	50°	78°	105°
Poisoned activity c.c. H_2/10 min.	13	12	12	7
Activity after washing	61	41	34	29
Activity after cyclohexene treatment	127	84	59	44
Activity after diethyl sulphide treatment and subsequent oxidation	—	122	108	86

Arsenious Oxide.—This poison was the most effective of those tested. Palladium, after being poisoned at 20°, was restored almost to its original activity on treatment with cyclohexene, whereas catalysts poisoned at 50°, 78°, and 105° were only partially reactivated, even by treatment with diethyl sulphide. These results are summarised in Table 5.

Recovery of activity by a palladium catalyst poisoned by lead acetate at 50°. I, Original activity. II, Activity of poisoned catalyst. III, Activity after washing. IV, Activity after treatment with cyclohexene. V, Activity after treatment with diethyl sulphide.

TABLE 5.

Arsenious oxide $= 5 \times 10^{-5}$ mole throughout.

Treated at	20°	50°	78°	105°
Poisoned activity c.c. H_2/10 min.	10	9	9	5
Activity after washing	54	28	22	14
Activity after cyclohexene treatment	123	63	51	34
Activity after diethyl sulphide treatment and subsequent oxidation	—	87	81	54

Palladium Supported on Thoria.—The thoria taken as the support was used as purchased, and the catalyst was made in bulk, in the ratio of 6 mg. of palladium to 2 g. of thoria, 2 g. of the catalyst being weighed out for each test.

In this part of the work, 2-g. samples of the supported catalysts were treated separately with various metallic acetates, in the concentration of 5×10^{-4} mole per batch, and kept at 150° for 15 hr.

The activity of the unpoisoned supported catalyst was determined separately at 20°, in the presence of the charge already described, the amount of the hydrogen absorbed in the first 5 min. being taken as a measure of the activity.

The catalyst samples, after being poisoned at 150°, were cooled and their activity tested at 20°. The remainder of the samples were then treated by the procedure already described, except that the amounts of cyclohexene, diethyl sulphide, permolybdic acid, and hydrogen peroxide were doubled. It was found that none of these treatments was successful and that only a

partial restoration of the activity was obtained. These results are given in Table 6. In this case acetic acid was not used as a washing liquid on account of its attack on the support. The relative effectiveness of these poisons will be seen from this Table.

TABLE 6.

Poison $= 5 \times 10^{-4}$ mole throughout.

	Zinc acetate	Cadmium acetate	Lead acetate	Mercuric acetate	Arsenious oxide
Blank, c.c. of $H_2/5$ min.	201	—	—	—	—
Poisoned activity	16	13	9	8	2
Activity after washing	36	33	30	18	12
Activity after cyclohexene treatment	71	51	38	31	20
Activity after diethyl sulphide treatment and subsequent oxidation	142	121	96	91	45

The same sample of the catalyst was not re-used for more than one treatment, since it is well known that the activity centres are not constant, and that, even after complete desorption of the poison, the same activity value cannot be expected.

DISCUSSION

Although it cannot be said with certainty which of these poisons is the most toxic, the order of difficulty in the desorption of various toxic ions was found to be: As>Hg>Pb>Cd>Zn. Maxted and Ball [3] have noticed that Hg^{2+} is more toxic than Zn^{2+}; and Maxted and Moon [2] found that tetramethyl-lead is slightly less toxic than dimethylmercury, this not being in the order of their relative size.

From these measurements it can be seen that, as the temperature of the adsorption of the toxic ions is increased, the difficulty in the reactivation of the catalyst also increases. This may be due to greater poison-to-palladium bond strengths, it being known from chemisorption studies that the bonding strength increases with an increase in the temperature. On the other hand, since the catalyst samples were dried after 15 hours' treatment with the poisonous ions at 50°, 78°, 105°, and 150°, the poisonous cations became more firmly bonded to the catalyst, in place of remaining partially in the liquid medium, as is the case for treatments at 20°.

In discussing the relative toxicities of these cations towards palladium catalysts, it is known that toxicity is dependent on two factors, namely, (i) a size or effective individual coverage factor for each molecule or atom of poison in an adsorbed state, and (ii) the average length of stay of the adsorbed molecule or atom on the surface. With all poisons, the average life is relatively long compared with that of a normal adsorbed species; indeed it is by virtue of this length of its adsorbed life that a poison acts, even when it is present in traces only.

If the projectional area of each ion is considered in place of that of each atom of the metallic poisons, which is equivalent to the square of its radius multiplied by its valency, then a factor is obtained which coincides with the relative effectiveness of the toxic cations, as shown in the Table.

Metal	Atomic radius (r_a in Å)	Ionic radius (r_i in Å)	Probable effective valency n	$r_i^2 n$
Zn	1·31	0·83	2	1·37
Cd	1·48	1·03	2	2·12
Pb	1·46	1·32	2	3·48
Hg	1·48	1·12	2	2·50
As	1·21	2·2	3	14·52

Except in the case of lead, which has a greater projectional area than mercury, although it is slightly less toxic, the others are in agreement with their relative effectiveness, as shown in the last column.

In comparing the relative effectiveness of the various methods employed for the

reactivation of the catalyst, it was found that washing with various liquids is effective only for catalysts poisoned at low temperatures, and that, as the temperature of poisoning was increased, less reactivation by this method was obtained. It is probable that the looseness of the bonding of these cations to the surface of the catalyst poisoned at low temperatures leads to an easier removal of these from the catalyst surface by washing.

Treatment with cyclohexene was found to be even more effective, owing to the unsaturated nature of this compound, and also to mass action; *i.e.*, by the capacity for displacing minute quantities of toxic ions if the unsaturated substance is present in large quantities.

The relatively greater effectiveness of treatment with diethyl sulphide may be due to three factors: (i) a large molecular size compared with that of toxic cations; (ii) mass action; and (iii) greater bond-strength, owing to a longer adsorbed life than that of cyclohexene. It will be seen from the reactivation data given in the Table that, as the size of the poisonous cations is increased, less reactivation, even after treatment with diethyl sulphide, is obtained, showing that the greater size of the diethyl sulphide molecule (3·5 Å) than of cations, has some effect in displacing the cations from the catalyst surface. In reactivation at higher temperatures, *e.g.*, at 105° and 150°, even this method was found to be less effective; it is probable that the toxic ions, at these temperatures, are very strongly held to the more active sites on the catalyst and render these sites permanently inactive. The partial reactivation of the catalyst is probably due to the less-active sites, on which the poisonous cations are loosely held and are replaced, by mass action, by the diethyl sulphide molecule.

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