Read across justification for palladium substances

Palladium (II) substances

Acute ecotoxicity data are available for four Pd (II) substances (H_2Cl_4Pd, $Pd(NO_3)_2$, $Pd(HCO_3)_2$, and $PdCl_2(NH_3)_2$) for algae, invertebrates, and fish (except H_2Cl_4Pd). In addition EC10 (or NOEC) values are available from algal studies which are considered to be chronic endpoints. For all of these substances fish were less sensitive than invertebrates, which were in turn less sensitive than algae. A consistent pattern of toxicity to the three trophic levels has therefore been observed for all of the four tested palladium (II) substances, although the levels at which effects are observed differ for the different palladium substances, even when the toxicity is expressed on the basis of palladium rather than the test substance.

Algae (and presumably therefore also plants) are the most sensitive trophic level to palladium toxicity, although the sensitivity depends upon the particular palladium substance tested. This situation differs from that which is usually found for toxic metals, where the toxicity is due to the "available" concentration of the metal, and the toxicity of the metal is not influenced by the nature of the counter-ions (provided that they are not toxic). In the case of palladium the nature of the coordinating ligands does appear to have an effect on the toxicity, and complexes with chloro groups (e.g. diamminedichloropalladium and dihydrogen tetrachloropalladate) show greater toxicity than the other tested substances to the same trophic level (see Figure 1.1), although the reasons for this are unclear.

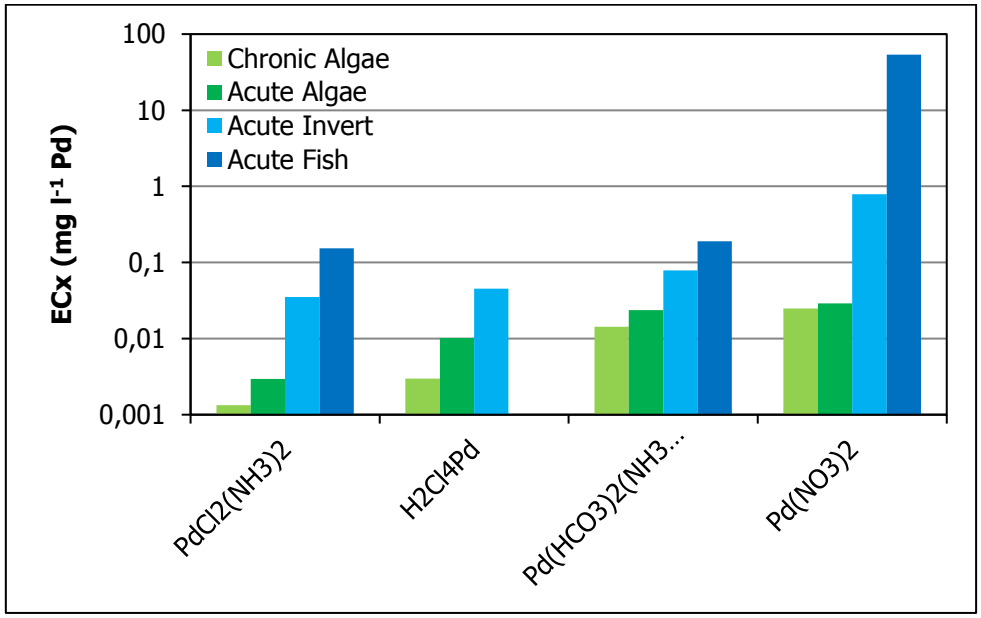


Figure 1.1 Sensitivity of ecosystem trophic levels to palladium (II) substances

The reasons for the sensitivity of algae to palladium are not clear although nickel, which is in the same elemental group as palladium, is known to be an essential element for plants (Brown et al. 1987), but not for animals. It is therefore possible that the presence of suitable biological uptake pathways for nickel results in increased sensitivity of plants to palladium.

The toxicity of the palladium substances, when expressed in terms of the palladium concentration, shows the same trend in toxicity to each of the three trophic levels tested (see Figure 1.2). Diamminedichloropalladium is consistently the most toxic of the tested palladium substances for all four of the available endpoints. Palladium nitrate is consistently the least toxic of the tested palladium substances.

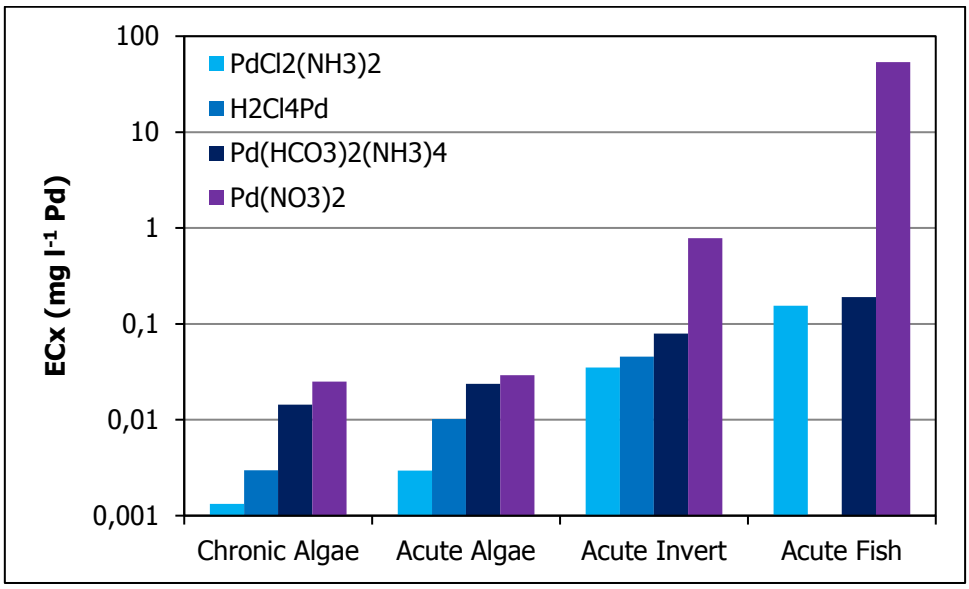


Figure 1.2 Ecotoxicity of palladium when present as different palladium (II) substances

In general the toxicity of metal compounds is considered to be due to the metal ions in solution, and the coordinating ligands or counter-ions are not expected to influence the toxicity unless they are themselves toxic. The differences which have been observed between the toxicity of the different palladium substances, when the exposures are expressed in terms of the palladium concentrations, suggests that this general approach cannot be applied to palladium substances.

The approach which is applied to palladium substances assumes that the palladium present in the environment has the potential to be in the most toxic form, which is diamminedichloropalladium. The generic PNEC for all palladium (II) substances is therefore based upon the ecotoxicity data for diamminedichloropalladium.

Palladium (IV) substances

Two palladium (IV) substances are being registered under REACH (diammonium hexachloropalladate and dipotassium hexachloropalladate). For the purposes of REACH registration these substances require acute ecotoxicity data for *Daphnia*, algae and fish. It is

proposed to read across ecotoxicity data available for diamminedichloropalladium, a palladium (II) salt, to satisfy these endpoint requirements for diammonium hexachloropalladate and dipotassium hexachloropalladate, both palladium (IV) salts.

Hexachloro palladium (IV) salts are only stable in the presence of strong oxidants, such as chlorine in aqueous solutions, which is how they are produced in Industry. In the absence of such oxidants the Pd (IV) substances decompose to the analogous palladium (II) tetrachloro salts. In the presence of strong hydrochloric acid Pd (IV) salts are capable of oxidising hydrochloric acid to chlorine gas, indicating that the Standard Redox Potential (E^o) of palladium (IV) must be greater than that of chlorine at 1.36V.

Chromium (VI) has a similar E^o of 1.33V, which has an extensive literature of environmental chemistry and persistence in the environment. However, significant differences exist between Cr (VI) and Pd (IV), in that the chromium (VI) salts can be isolated as stable entities and their solutions exhibit medium to long-term stability, whereas the Pd (IV) substances considered here cannot be isolated and will begin to spontaneously decompose in air (Pourbaix et al. 1959) and aqueous solutions (Griffith et al. 2008, Koltunov and Kostyukov 1995, De Filippo et al. 1969, Wellman 1930).

In common with other platinum group metals, palladium is very reactive towards nitrogen and particularly sulphur containing moieties in biological systems (Kornblum's rule; Kornblum et al. 1955), inevitably with *in situ* reduction to palladium (II), leading to further degradation pathways in such systems.

No data were found that describe the kinetics or products of Pd (IV) reduction in biological or environmental systems. Therefore, analogy is made with data provided from laboratory studies by Wellman (1930), and others, who concluded that for hexachloro palladium (IV) in 1M hydrochloric acid, 'little', tervalent (sic) Pd was found in the equilibrium mixture. Koltunov and Kostyukov (1995) found that for low chloride concentrations in nitric acid solutions, the reduction proceeded autocatalytically due to the release of chloride by decomposition of the hexachloro palladium (IV).

The reduction of hexachloro palladium (IV) by 2,6-pyridinedihydroxamic acid was studied by Griffith et al. (2208), who concluded that the reaction products were the analogous 2,6-pyridinedihydroxamato Pd (II) complexes. De Filippo et al. (1969) found that hexachloro palladium (IV) was reduced in aqueous solutions in the presence of 3-thiomorpholinone (T) to form a series of Pd (II)-T complexes by progressive hydrolytic anation of the chloro ligands.

The above studies were conducted in strong acid solutions and are, therefore, not directly applicable to more environmentally relevant conditions. Since no data could be found describing the kinetics of hexachloropalladate (IV) in neutral to weak acid solutions, experimental data were generated at Johnson Matthey Technology Centre. The results are presented as an Appendix to this document and suggest that in 0.1M HCL the half-life of the Pd (IV) hexachloro anion is 168 seconds. The half-life could not be determined for neutral solutions due to the formation of a fine precipitate, but it is anticipated that the rate of reaction would be intrinsically faster in neutral solutions.

It is therefore concluded that Pd (IV) will not survive in biological and environmental systems due to its inherent instability, ease of reduction and its ability to reductively form strong complexes with organic nitrogen and sulphur containing moieties.

OECD guidance (OECD 2000) on testing suggests that for substances which degrade in the test system, the substance which is effectively tested (with 24 hour medium renewals) depends upon the half life of the parent substance in the test system. The following guidelines are given:

- Half-life >3 days: test parent substance;
- Half-life <3 days and >1 hour: consider on a case-by-case basis, and include possible testing of degradation products;
- Half life <1 hour: test degradation products.

For risk assessment, PECs and PNECs should relate to the same compound(s). For example, the degradation half-life should be compared with the duration of the emission and the time taken for the emission to reach the receiving water. If degradation is rapid, only the degradation product(s) are important (ECHA 2008).

Summary of ecotoxicity read-across approach for all palladium substances

Ecotoxicity data are available for four palladium (II) substances:

- Dihydrogen tetrachloropalladate
- Tetraammine palladium hydrogen carbonate
- Palladium dinitrate
- Diamminedichloropalladium.

The data suggest that compounds containing chloro groups may be more toxic than other palladium substances. Dihydrogen tetrachloropalladate exhibits a similar level of toxicity to diamminedichloropalladium, whereas tetraammine palladium hydrogen carbonate and palladium dinitrate both exhibited lower toxicity than the chloro-complexes to all three trophic levels (see table below).

Test	Palladium dinitrate	tetraammine palladium hydrogen carbonate	Dihydrogen tetrachloro palladate	Diammine dichloro palladium
	mg Pd/L	mg Pd/L	mg Pd/L	mg Pd/L
Acute Algae	0.029	0.024	0.010	0.003
Acute Invert	0.785	0.079	0.045	0.035
Acute Fish	53.569	0.190	NA	0.154

Read across of environmental fate and effects endpoints from diamminedichloropalladium is therefore proposed as a 'worst case' scenario for all of the Pd(II) and Pd(IV) substances. This is justified because of the extremely short half-life of Pd (IV) species in aqueous systems (< 3 minutes), which means that any emissions of palladium (IV) substances will

not result in the exposure of ecosystems to Pd (IV) because the reactive Pd (IV) species will have been reduced to Pd(II) species. This approach is consistent with the OECD (2000) guidance on ecotoxicity testing of difficult substances, as the half-life of Pd (IV) species is much less than 1 hour.

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Appendix

The reduction of hexachloropalladate $[PdCl_6]^{2-}$ in 0.1 M hydrochloric acid (HCl)

Dr. John Wells

Introduction

The Pd (IV) complex $[PdCl_6]^{2-}$ is known to auto-reduce in aqueous solution to form Pd (II) species and Cl_2 gas. This reaction is employed industrially in the refining of palladium metal. The $[PdCl_4]^{2-}/[PdCl_6]^{2-}$ couple is reported to be a 1.288 V relative to the normal hydrogen electrode.

However the rate at which this reduction occurs has not been reported in the literature. The half-life of decomposition of $[PdCl_6]^{2-}$ to Pd (II) species is of importance when considering the toxicology of the Pd (IV) complex. An experiment was therefore conducted to determine the rate at which this species decomposes in 0.1 M HCl at 25 °C.

Experimental Design

A quartz cuvette was filled with 0.1 M HCl and placed inside a UV/vis spectrometer equipped with a thermostatically controlled cuvette holder. The solution was allowed to heat to 25 °C and a background spectrum taken. A small quantity of diammonium hexachloropalladate $(NH_4)_2[PdCl_6]$ was dissolved in the solution and the spectrum recorded.

For kinetic measurements, a quartz cuvette was filled with 0.1 M HCl and placed inside a UV/vis spectrometer equipped with a thermostatically controlled cuvette holder. The solution was allowed to heat to 25 °C and a zero reading taken. A small quantity of $(NH_4)_2[PdCl_6]$ was dissolved. The decay of the adsorption at 335 nm was recorded over a period of 1300 seconds, with data points being measured at 0.5 second intervals.

Results and Discussion

Attempts to measure the rate at which $[PdCl_6]^{2-}$ reduced in water were complicated by the formation of a fine precipitate, which interfered with the accumulation of UV/vis data. The measurements were therefore conducted in 0.1 M HCl, which was found to solubilise the Pd products formed. However, the rate at which the decomposition occurs should not be significantly different in water than 0.1 M HCl; indeed, it should be faster.

The spectrum of $[PdCl_6]^{2-}$ in 0.1 M HCl is shown in

Figure 1.

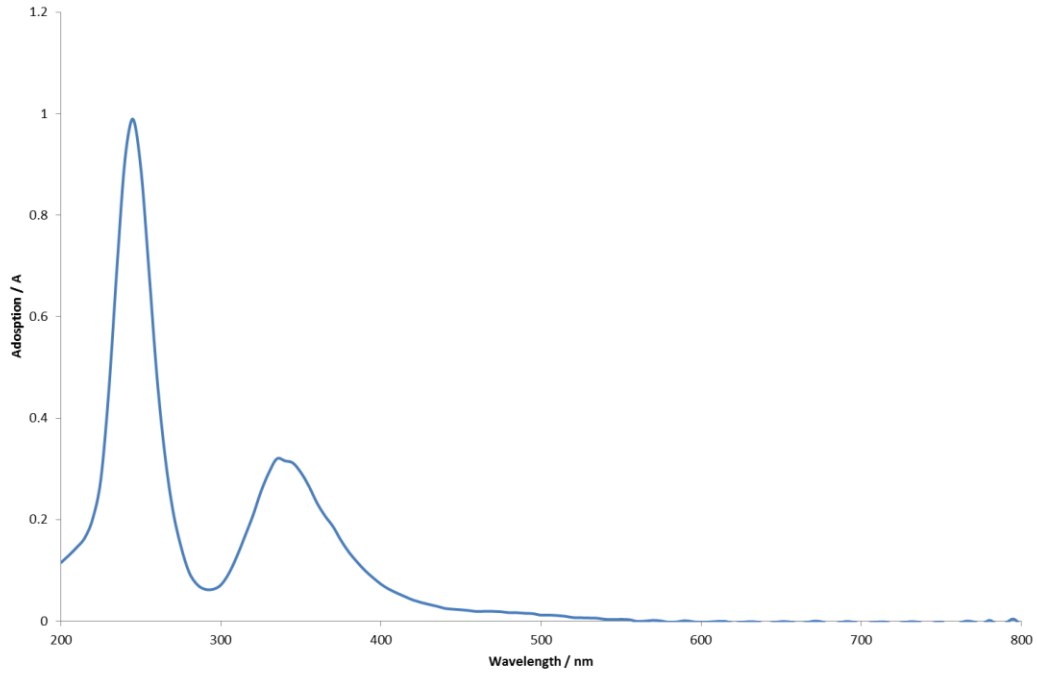


Figure 1: ` UV/vis spectrum of $[PdCl_6]^{2-}$ in 0.1 M HCl

The λ_{max} was observed at a wavelength of 335 nm. The decay of this band was monitored with respect to time. After a period of 15 minutes there was no further change in the adsorption at this wavelength, indicating the complete decomposition of $[PdCl_6]^{2-}$. The speciation of the decomposition products was not investigated. Gas bubbles were observed to have formed inside the cuvette during the reaction and the distinct smell of chlorine gas was noted.

A plot of adsorption *vs.* time (Figure *2*) over the first 10 minutes of reaction was well fitted to exponential, indicating first order behaviour with respect to $[PdCl_6]^{2-}$.

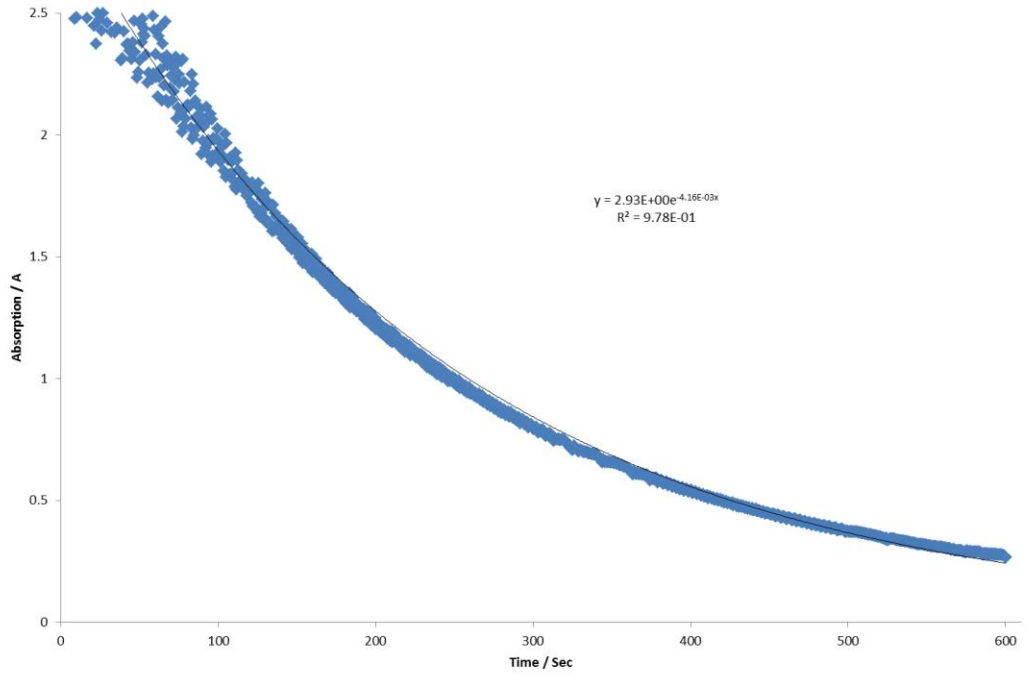


Figure 2: Absorption (335 nm) vs time (seconds) for the decomposition of $[PdCl_6]^{2-}$ in 0.1 M HCl

Plotting the natural logarithm of absorption against time gave a linear plot, confirming the first order dependence (Figure 3).

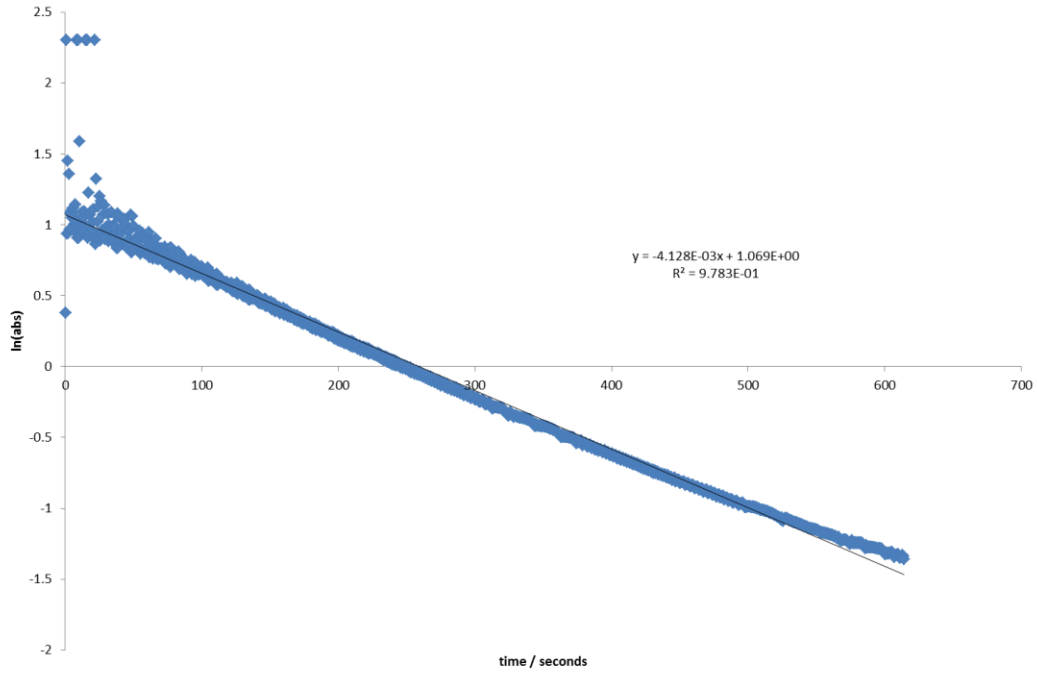


Figure 3: ln(abs) at 35 nm vs time (seconds) for the decomposition of $[PdCl_6]^{2-}$ in 0.1 M HCl

From these data, the pseudo first order rate constant at 25 °C was determined to be 4.13 x 10^{-3} s^{-1}. The half-life of reaction was therefore $t_{1/2}$ = 168 seconds.