Rhenium Compounds for REACH

Speciation and Read Across

Preliminary Report

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Bioavailability, Speciation and Read Across

Rhenium substances for REACH are rhenium metal Re, perrhenic acid $HReO_4$, ammonium perrhenate NH_4ReO_4 , rhenium heptoxide Re_2O_7 , sodium perrhenate $NaReO_4$ and rhenium heptasulfide Re_2S_7. Our concern is the toxicity and environmental impact of these substances. For a compound to be able to enter biology, i.e. to be *bioavailable,* it must be soluble in water. The *bioavailability* is related to *solubility:* the more soluble, the more bioavailable.

Our concern is also with the *chemical species* in solution when a compound has dissolved: their composition, charge, and structure, with *speciation*. A cell will select a species to take up. For example, for molybdenum it is the molybdate ion. However, we may not know what species is preferentially taken up; the amount dissolved is then the maximum amount which can be taken up.

Knowing the speciation will also help us to *read across* from one substance to another in a REACH assessment. If a number of substances give rise to the same species then they will have the same biological impact: having tested one substance we can assign the same properties to other substances. This is the principle of *read across*. (A caveat: a substance ingested as a powder, e.g. by inhalation, may have a biological impact as a consequence of its particulate nature. I am not considering this here.)

The purpose of this Report is to describe how understanding the chemistry of rhenium and the properties of rhenium compounds will enable us to justify read across in the REACH assessment. I summarise the rhenium chemistry of interest, the solubilities of rhenium compounds, and their speciation in water. The Report is preliminary because I have not yet been able to obtain and review all relevant papers.

Rhenium Chemistry

Rhenium is the third vertical member of Group 7 of the Periodic Table. For rhenium the +7 oxidation state is stable; familiar compounds are compounds of Re(VII), for example the oxide Re_2O_7 and salts of the perrhenate ion, $[ReO_4]^-$.

Rhenium resembles molybdenum, the second member of Group 6 of the Periodic Table. For example, familiar compounds of molybdenum are those of the highest oxidation state, +6 (MoO_3 and molybdates). Molybdenum and rhenium are said to have

a diagonal periodic relationship and comparison of their chemistries can be profitable.

The aqueous chemistry of rhenium-oxygen compounds is dominated by the very stable anion of rhenium in its highest oxidation state, perrhenate, $[ReO_4]^-$. The $[ReO_4]^-$ ion is the anion of the strong monobasic acid, perrhenic acid, $HReO_4$. The $[ReO_4]^-$ ion is stable in acidic and basic solution and does not polymerise, in contrast to the molybdate and tungstate anions.

Rhenium(VII) as Re_2O_7 or a perrhenate salt is the ultimate product of the oxidation or rhenium compounds. Pertinent observations (N. V. Sidgwick, The Chemical Elements and Their Compounds, Oxford, 1950, Vol. 2, p. 1262) are

- Rhenium metal and ReO_2 heated in air or oxygen yield Re_2O_7 . Finely divided rhenium metal is said to be pyrophoric.
- The sulfide Re_2S_7 heated in air oxidises to Re_2O_7.

Potassium perrhenate unlike potassium permanganate is thermally stable: $KReO_4$ melts without decomposition at 518 °C while $KMnO_4$ loses oxygen at 200 °C.

Perhenate is reduced by, for example Ti(III), Fe(II), and Sn(II). For example, an older colorimetric analytical method for rhenium is reduction of perrhenate by tin(II) chloride, followed by addition of thiocyanate, NCS^-, to give a colored Re(V) thiocyanate complex (cf. molybdate) (N. H. Furman (ed.), Standard Methods of Chemical Analysis, van Nostrand, 1962, p. 915). However, perrhenate is less easily reduced than, for example, permanganate (a powerful oxidizing agent). For example

- The oxide Re_2O_7, dissolves in ethanol and does not oxidise ethanol.
- Perrhenate in water reacts with hydrogen sulfide forming a thioperrhenate, $[ReO_3S]^-$. When this solution is acidified with hydrochloric acid the sulfide, Re_2S_7 precipitates. (Analogous to molybdate.)

The ability of a species to behave an as oxidising or reducing agent (its redox chemistry) is quantified by the standard reduction potentials. These are listed in Table 1 for the Re(VII)/Re(IV) couple and compared with permanganate and molybdate: the more positive potential, the more oxidising the couple or the easier the reduction of the higher oxidation state. We see that in its redox chemistry rhenium resembles molybdenum rather than manganese (the first member of Group 7).

Table 1 Reduction potentials, E^o/V, of perrhenate compared with permanganate and molybdate

Couple	Acidic solution	Basic or neutral solution

$[ReO_4]^-/ReO_2$	0.51	−0.594
$[MnO_4]^-/MnO_2$	1.69	0.60
$[MoO_4]^{2-}/MoO_2$	0.646	−0.780
D. F. Shriver, P. W. Atkins and C. H. Langford, Inorganic Chemistry, Oxford, Second Edition 1994.		

Rhenium Compounds in Water — Solubilities and Speciation

Solubilities

Literature data on the solubilities of rhenium compounds are given in Table 2.

Table 2 Water solubility of rhenium and rhenium compounds

Substance				Solubility in water				Literature	Notes
name	formula	molar mass	CAS number	t/°C	g substance /100 water	g Re /100 g water	mol Re /L		
rhenium	Re	186.2	7440-15-5	25		1.4×10^{-5}	8×10^{-7}	Kim et al. 2003	Surface layer of ReO_2 dissolves
						2×10^{-8}	1×10^{-10}	Xiong et al. 2006	
perrhenic acid	$HReO_4$	251.2	13768-11-1		very soluble'			Perry and Phillips 1995a	
								Bailey et al. 1960	uv spectra and pK -1.25. No solubilities.
							>7	Carrington et al. 1957	uv. No solubility
								Covington et al. 1969	uv, Raman, pmr. No solubility.
ammonium perrhenate	NH_4ReO_4	268.2	13598-65-7	20	slightly soluble'			Perry and Phillips 1995b	
				20	6.23	4.33	0.23	Lewino 1932	
					6.17	4.28	0.23	Feit 1931	
					5.84	4.05	0.22	Shkodina et al. 1984	
				25	12.07	8.38	0.45	Noddack and Noddack 1933	
					6.92	4.80	0.26	Shkodina et al. 1984	
					7.35	5.10	0.27	Johnson 1990	
				30	8.72	6.05	0.33	Smith 1946	
rhenium heptoxide	Re_2O_7	484.4	1314-68-7		very soluble'			Perry and Phillips 1995c	
sodium perrhenate	$NaReO_4$	273.2	13472-33-8	20	94.25	64.24	3.45	Vayenas 2008	
				20	100.00	68.16	3.66	Perry and Phillips 1995d	
rhenium heptasulfide	Re_2S_7	596.9	12038-67-4		insoluble'			Perry and Phillips 1995e	

Kim et al. 2003 E. Kim and J. Boulegue, Radiochim. Acta,, 2003, 91, 211 – 216.
Xiong et al. 2006 Y. Xiong, S. Wood and J. Kruszewski, Econ. Geol., 2006, 101, 471 – 478.
Perry and Phillips 1995a D. L. Perry, S. L. Phillips (eds.), Handbook of Inorganic Compounds, CRC Press, 1995, p. 291.
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Noddack and Noddack 1933 I. Noddack and W. Noddack, Das Rhenium, Leipzig, 1933, S. 50.
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Perry and Phillips 1995c D. L. Perry, S. L. Phillips (eds.), Handbook of Inorganic Compounds, CRC Press, 1995, p. 330.
Vayenas 2008 C. Vayenas, Modern Aspects of Electrochemistry, Springer, 2008, p. 273.
Perry and Phillips 1995d D. L. Perry, S. L. Phillips (eds.), Handbook of Inorganic Compounds, CRC Press, 1995, p. 374.
Perry and Phillips 1995e D. L. Perry, S. L. Phillips (eds.), Handbook of Inorganic Compounds, CRC Press, 1995, p. 330.

Sodium perrhenate is the most soluble compound (90 – 100 g compound in 100 g water, 3.5 – 3.7 M Re) and is more soluble than, for example, sodium molybdate dihydrate (40 g in 100 g water, 1.7 M Mo). Perrhenic acid and rhenium heptoxide are described as 'very soluble' but no values are available. Both compounds give the $[ReO_4]^-$ ion in water. The solubility of ammonium perrhenate is less than 10% the solubility of sodium perrhenate and rhenium heptasulfide is described as 'insoluble'.

Speciation

The speciation of perrhenic acid in water has been investigated. Perrhenic acid $HReO_4$ is a strong acid completely ionised in water up to concentrations of 7 mol L^{-1}.(A. K. Covington , G . Freeman and T. H. Lilley, Trans. Faraday Soc.,1969, 3138). The $[ReO_4]^-$ ion is the only rhenium species in perrhenate solutions at concentration 10^{-3} mol L^{-1} and pH 4 and 10 (Craig S. Truebenbach , Marwan Houalla , David M. Hercules, J. Mass Spectrometry, 2000, 35, 1121–1127). The $[ReO_4]^-$ ion has a characteristic uv spectrum (like molybdate) which can be used for its characterisation. The aqueous solution chemistry of perrhenate is simpler than molybdate since perrhenate does not protonate or polymerise. It is reasonable to assume that the $[ReO_4]^-$ ion is the species in solutions of rhenium heptoxide, ammonium perrhenate, and sodium perrhenate.

Rhenium metal, as sheet or powder, is covered with a layer of rhenium(IV) oxide, ReO_2 (by x-ray photoelectron spectroscopy, XPS: Y. Xiong, S. Wood and J. Kruszewski, Econ. Geol., 2006, 101, 471 – 478). Dissolution is thus the reaction of ReO_2 with water:

$ReO_2(s) + 2H_2O(l) = Re(OH)_4(aq)$.

The rhenium(IV) species in water are uncharged: $Re(OH)_4$ or $ReO(OH)_2$. Because of the low solubility of ReO_2 (10^{-6} M) the amount of rhenium which goes into solution from rhenium metal is also small (10^{-8} M, Table 2).

The dissolution of ReO_2 and Re_2O_7 has been investigated (E. Kim and J. Boulegue, Radiochim. Acta,, 2003, 91, 211 – 216) and the regions of stability of Re(IV) and Re(VII) aqueous species are shown on E_h/pH diagrams for rhenium concentrations of 10^{-8} and 10^{-5} M under oxic and anoxic conditions. (E_h is a reduction potential). Under oxic conditions (i.e. in air or oxygen) perrhenate is the stable species from both ReO_2 and Re_2O_7.

To summarise: the indications are that rhenium powder, rhenium heptoxide and perrhenates all give the simple $[ReO_4]^-$ ion in water over a range of acidic, neutral and basic pH and all concentrations.

There remains the question of what species are formed from rhenium heptasulfide in contact with water. We can speculate that rhenium heptasulfide is covered with a layer of oxide and that the species ultimately formed in water would be perrhenate (cf molybdenum disulfide which is covered with layer of molybdenum trioxide and gives molybdate with water).

Read Across

This survey of rhenium chemistry and the properties of rhenium compounds indicates that the $[ReO_4]^-$ ion will be the dominant species in water in contact with the compounds of interest for REACH assessment. We can undertake biological testing on the most soluble compound, sodium perrhenate, and then read across to the other substances.

We need to consider whether our view that our rhenium substances all yield the $[ReO_4]^-$ ion in water is sufficiently well founded for REACH or whether we need to show this experimentally for each substance. This could be done by measuring the uv spectra of each substance dissolved in or in contact with water — as for molybdenum compounds.