

REACTION IN Re(VII) – Sn(II) – HCl SYSTEM

V.Koltunoy, T.Gomonova

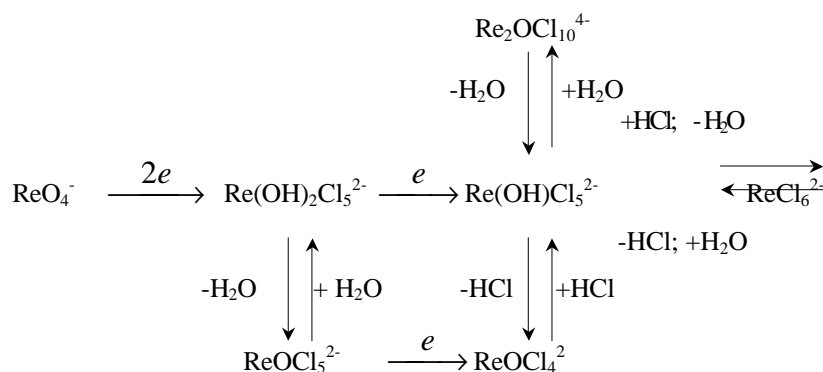
FSUE VNIINM, Moscow p/b 369, Russia

The technology of producing radiopharmaceutical preparations containing Re-186 or Re-188 radionuclides is based on the synthesis of complex compounds of some organic ligands with ions of lower valence Re. In this case Sn(II) in HCl solution is often used as a reductant.

In view of this fact of interest are data on the stoichiometry, products and kinetics of Re(VII) – Sn(II) reaction. The analysis of results available in literature and those acquired by the authors reveals that in the Re(VII) – Sn(II) – HCl system oxidation-reduction transformations of Re(VII) → Re(V) and Re(V) → Re(IV) are simultaneously attended with aquatation, hydrolysis, anation, disproportionation, reproporation and dimerization of Re(V) and Re(IV) ions; because of the inertness of the ligand exchange of those Re valences the reactions proceed at a rather low rate.

The general schematics of the reactions in the Re(VII) – Sn(II) – HCl system is illustrated in fig.1; it is obvious from the figure that at least 7 successive and parallel reactions proceed upon Re(VII) – Sn(II) interaction.

Fig.1 The general schematics of the reaction in the Re(VII) - Sn(II) – HCl system



Despite the intricate reaction as a whole it is still possible to investigate the kinetics of its individual stages due to substantial differences in the absorption spectra of the ion forms of Re(VII), Re(V) and Re(IV) and the extinction coefficients of those forms in the characteristic absorption maxima (table 1).

The first reaction that takes place in the system upon mixing solutions of HReO₄ and Sn(II) involves a quick Re(VII) → Re(V) reduction

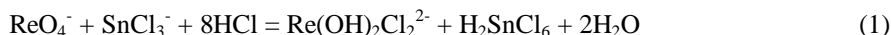


Table 1. Extinction Coefficients of Re Ions in HCl Solutions.

Re valence	Re ion Form	[HCl], M	200-300 nm		300-400 nm		450-700 nm		700-800 nm	
			λ nm	ε M ⁻¹ cm ⁻¹	λ nm	ε M ⁻¹ cm ⁻¹	λ nm	ε M ⁻¹ cm ⁻¹	λ nm	ε M ⁻¹ cm ⁻¹
VII	ReO ₄ ⁻	1	206 230	6060 3600						
V	Re(OH) ₂ Cl ₅ ²⁻	4			395	60			752	22
V	ReOCl ₅ ²⁻	4			395	26				

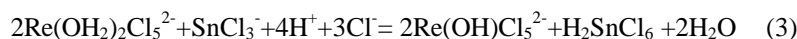
		10	241	6350	414	30	481	33	797	24
IV	Re(OH) ₂ Cl ₅ ²⁻	11	269	5700					720	110
IV	ReOCl ₄ ²⁻	4			341	5200	609	90		
IV	ReCl ₆ ²⁻	11	281	11800	350	20	640	2	710	3
IV	Re ₂ OCl ₁₀ ⁴⁻	2	250	10000	330	13000	610	200		
					350	15000	640	150		

The reaction is fully completed during the time of mixing the reagents and at their equivalent-concentrations the reaction product is Re(OH)₂Cl₅²⁻ ions that feature the maximum absorption at 752nm at the extinction coefficient $\epsilon \approx 22\text{M}^{-1}\text{cm}^{-1}$ (in 4M HCl) and a plateau at $\lambda = 395\text{nm}$ at $\epsilon \approx 60\text{M}^{-1}\text{cm}^{-1}$. Under the above conditions as well as with a shortage of Sn(II) the subsequent Re(V) \rightarrow Re(IV) reduction is not observed, however, Re(OH)₂Cl₅²⁻ dehydration takes place:



attended by a decrease of the absorption in the range of 395 nm and the plateau transformation to the maximum at $\epsilon \approx 26\text{M}^{-1}\text{cm}^{-1}$. Reaction (2) obeys the first order equation at the rate constant $k_1 = 8.2 \times 10^{-2}\text{min}^{-1}$, [HCl] = 4M and 25°C. The reaction accelerates as the concentration of HCl increases and in 10M HCl it takes 1 or 2 min at 25°C for it to be fully complete. Due to this fact the final product of the Re(VII) – Sn(II) interaction in strong solutions of HCl is ReOCl₅²⁻ ions having maxima at 241 nm ($\epsilon = 6350\text{M}^{-1}\text{cm}^{-1}$), 414nm ($\epsilon \approx 30\text{M}^{-1}\text{cm}^{-1}$), 481 nm ($\epsilon \approx 33\text{M}^{-1}\text{cm}^{-1}$) and 797 nm ($\epsilon \approx 24\text{M}^{-1}\text{cm}^{-1}$).

In excess Sn(II) both the forms of Re(V) are reduced to Re(IV):



to form, respectively, Re(OH)Cl₅²⁻ ions with the maxima at 269 and 720 nm and ReOCl₄²⁻ ions with the maxima at 341 and 609 nm (see table 1). The rates of reactions (3) and (4) differ substantially and obey kinetic equations of different forms. For reaction (3) the rate equation was derived:

$$-d[\text{Re(V)}]/dt = k_2[\text{Re(OH)}_2\text{Cl}_5^{2-}] / [\text{H}^+] \quad (5)$$

where $k_2 = (9.0 \pm 0.2) \cdot 10^{-2}\text{M} \cdot \text{min}^{-1}$ at 40 °C and the ionic strength of the solution $\mu = 2$. The reaction is of the zero order in relation to Sn(II). The kinetics of reaction (4) was studied in a greater detail. In this instance the rate equation assumes the form of

$$-d[\text{Re(V)}]/dt = k_3[\text{ReOCl}_5^{2-}][\text{Sn(II)}] / [\text{HCl}] \quad (6)$$

where $k_3 = 4.52 \pm 0.18\text{min}^{-1}$ at 25°C and variable ionic strength. The activation energy of this reaction is $E_3 = 47.6 \pm 0.8\text{kJ/mole}$. Some data on reaction (3) kinetics are given in table 2.

Table 2. First Order Rate Constants vs Concentrations of Sn(II) and HCl

[HCl] M	[Sn(II)] 10 ² , M	$k' \cdot 10^2$, min ⁻¹	k_3 *) min ⁻¹	[HCl] M	[Sn(II)] 10 ² , M	$k' \cdot 10^2$, min ⁻¹	k_3 min ⁻¹
4.0	1.0	1.3	5.20	4.0	7.5	8.8	4.68
4.0	2.5	3.3	5.28	3.5	5.7	6.1	4.41
4.0	4.0	4.3	4.32	4.0	6.6	7.9	4.36
4.0	5.0	5.7	4.56	4.9	6.6	5.9	4.38
4.0	6.1	6.7	4.40	5.8	13.2	91	4.00
4.0	6.6	7.9	4.36			mean	4.52 ± 0.18

ReOCl_4^{2-} ions that form in the course of reaction (4) are stable in 4M HCl solution, however, with an increase in [HCl] one observes a slow reaction of anation to form Re(OH)Cl_5^{2-} ions:



at the rate constant $k_4' = 8.0 \pm 10^{-2} \text{ min}^{-1}$, 25°C and $[\text{HCl}] = 11.3\text{M}$. In this instance the absorption of ReOCl_4^{2-} ions at 341 nm decreases while the absorption of Re(OH)Cl_5^{2-} ions at 269 nm increases. Reaction (7) is reversible and at a low acidity it proceeds in the opposite direction. Fully coordinated ion $\text{Re(IV)} - \text{ReCl}_6^{2-}$ having the absorption maximum at 281 nm is formed in strong solutions of HCl at an elevated temperature via the reaction of Re(OH)Cl_5^{2-} anation:



The rate constant of the reaction is $k_5' = 3.6 \times 10^{-2} \text{ min}^{-1}$ at 90°C and $[\text{HCl}] = 11.3\text{M}$. Of special interest is reversible reaction (8), proceeding as the concentration of HCl is lowered down.

In conclusion, it is to be pointed out that despite the complex and multistage character of the $\text{Re(VII)} - \text{Sn(II)}$ reaction in the HCl solution it is feasible to prepare rhenium in the needed valence and ionic form making use of the difference between the rates of individual stages of the reaction and between their dependences on temperature and concentrations of Sn(II) and HCl.