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CHEMISTRY

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RHENIUM-THIOUREA COMPLEX COMPOUNDS

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Thiourea has found wide application in analytical chemistry for the quantitative determination of a number of elements: Cu, Zn, Cd, Hg, Tl, Pb, Bi, Os, Ru, Mn^{4+}, BrO_3^-, ClO_3^-, CrO_4^{2-}, NNO_2^-, etc. ([1–3]). This reagent was first used in 1955 ([4]) for the determination of rhenium in the form of a yellow-green complex compound with an absorption maximum at 390 mμ, formed when excesses of the reagents—thiourea and $SnCl_2$—are mixed. We have established that rhenium with thiourea forms, in addition to the already known compound, a number of complex compounds having different colors.

The known compound with a light-absorption maximum at 390 mμ is obtained in dilute HCl solutions (1.5–6 N) when $HReO_4$, a considerable excess of thiourea, and $SnCl_2$ are mixed in amounts corresponding to a molar ratio Re : Sn $\leqslant$ 1 : 1.5 (Fig. 1a). When the concentration of HCl is increased to 7–8 N, and with the same reagent ratios as above, an orange-red complex compound is formed with a light-absorption maximum at 420 mμ (Fig. 1, b).

The minimum amount of $SnCl_2$ required for the formation of each of these two compounds is 1.5 moles of $SnCl_2$ per 1 mole of $HReO_4$, whence it follows that the valence of rhenium in them is equal to four*. With a larger number of moles of $SnCl_2$ per 1 mole of $HReO_4$, the same compounds are formed. This circumstance indicates that compounds with a rhenium valence lower than four, in the presence of excess $SnCl_2$, apparently are not formed.

Fig. 1. Absorption spectra of rhenium thiourea complex compounds. *a*–1.5–6 N HCl, $SnCl_2$–large excess; *b*–7–8 N HCl, Re : Sn = 1 : 1.5, max. = 420 mμ; *v*–1.5–6 N HCl, Re : Sn = 1 : 1, max. = 520 mμ; *g*–7–8 N HCl, Re : Sn = 1 : 1, max. = 570 mμ

Entirely different compounds are obtained at molar ratios Re : Sn $\geqslant$ 1 : 1. In 1.5–6 N HCl, when solutions of $HReO_4$ are mixed with excess thiourea and $SnCl_2$ in amounts corresponding to a molar ratio in moles Re : Sn = 1 : 1, a compound is

Fig. 2. Change in the absorption spectra of the "blue" and "pink" rhenium compounds with thiourea upon dilution with water in 11 N HCl. a–7-8 N HCl, Re : Sn = 1 : 1; b–solution a diluted with water; c–6 N HCl, Re : Sn = 1 : 1; d–solution c to which 11 N HCl has been added

Figure 1: Fig. 2. Change in the absorption spectra of the "blue" and "pink" rhenium compounds with thiourea upon dilution with water in 11 N HCl. a–7-8 N HCl, Re : Sn = 1 : 1; b–solution a diluted with water; c–6 N HCl, Re : Sn = 1 : 1; d–solution c to which 11 N HCl has been added

formed that is colored bright pink, with a light-absorption maximum at 520 mμ (Fig. 1, v) and maximum intensity in 6 *N* HCl. Under the same conditions, but in 7–8 *N* HCl, a "blue" compound is formed with a light-absorption maximum at 570 mμ (Fig. 1, g).

* The same is noted by Beckman and Lederer ([7]) for the yellow-green compound.

The molar ratio Re : Sn = 1 : 1, necessary for the formation of these compounds, indicates that the valence of rhenium in them is five.

When an excess of concentrated HCl is added to a solution of the compound colored pink, the color changes from pink to blue and, conversely, when water is added to a solution of the "blue" compound the color changes to pink, with the absorption spectra likewise changing from one type to another (Fig. 2). From the data presented it is evident that, depending on the conditions under which the reaction is carried out–the acidity of the medium and the molar ratios Re : Sn–at least four compounds are formed.

Fig. 2. Change in the absorption spectra of the "blue" and "pink" rhenium compounds with thiourea upon dilution with water in 11 N HCl.
a–7-8 N HCl, Re : Sn = 1 : 1; *b*–solution *a* diluted with water; *c*–6 N HCl, Re : Sn = 1 : 1; *d*–solution *c* to which 11 N HCl has been added.

Let us consider the blue compound in somewhat greater detail. It is obtained by mixing 0.01-0.1 M solutions of $HReO_4$ with an excess of thiourea and $SnCl_2$ in amounts corresponding to a molar ratio Re : Sn $\geq$ 1 : 1, reaching maximum intensity in 8 N HCl at the ratio Re : Sn = 1 : 1 (Table 1).

As can be seen from the data in Table 1, in all cases when $HReO_4$ and $SnCl_2$ are mixed in molar ratios Re : Sn $\geq$ 1 : 1, a compound is formed with an absorption maximum at 570 mμ. But already at the ratio Re : Sn = 1 : 1.5 a compound is formed with an absorption maximum at 420 mμ, as was indicated above. Other data in Table 1 are especially interesting. As can be seen, during the first 30 min after mixing the reagents the densities of the "blue" solutions are not identical, and the maximum intensity corresponds to the solution where Re : Sn = 1 : 1. After one day the optical-density values become equal, reaching 0.48.

Table 1

Dependence of optical density on the Re : Sn ratio with time (thiourea everywhere 1 ml of 1 M solution, total acidity 8 N HCl, total volume –const)

No.	$HReO_4$, 0.02 M, ml	$SnCl_2$, 0.02 M, ml	Re : Sn	Color of solution	Absorption maximum, mμ	Optical density after mixing the reagents, after 30 min	Optical density after mixing the reagents, after 1 day
1	1	–	–	Blue	570	0.12	0.48
2	1	0.25	1 : 0.25	Blue	570	0.27	0.48
3	1	0.5	1 : 0.5	Blue	570	0.44	0.48
4	1	1	1 : 1	Blue	570	0.48	0.48
5	1	1.5	1–1.5	Yellow-brown	420	–	–

This indicates the circumstance that the amount of $SnCl_2$ (within the limit Re : Sn $\geq$ 1) does not affect the final value of the optical density, but does affect the rate of development of the coloration. It follows from this that thiourea itself, which is known[(5)] to possess reducing properties in acidic media, also plays the role of reducing agent. Experimental data confirmed our supposition, namely,– when mixing

With $HReO_4$ and thiourea, without $SnCl_2$, under otherwise identical conditions (Table 1, no. 1), the formation of the "blue" compound was observed. However, reduction by thiourea proceeds very slowly, so that the solution reaches maximum intensity only after 24 hours. In this case thiourea performs a dual function–as reducing agent and as complexing agent.

From the data presented it follows that the overall rate of formation of the compound, which depends on the rate of reduction of rhenium and the rate of complex formation, under our specific conditions depends mainly on the rate of reduction of rhenium and increases upon addition of a foreign reducing agent– $SnCl_2$.

Moreover, from the data presented it follows that thiourea reduces rhenium to the pentavalent state under our conditions. Figure 3 shows the obedience of the "blue" solutions to the Lambert-Beer law both in the presence and in the absence of $SnCl_2$. It follows from this that analytical determinations of rhenium can be carried out using the "blue" compound, with additions of $SnCl_2$, as is done in the determination of Os and Ru[^6] by the thiourea method.

Fig. 3. Dependence of the optical density of solutions of the "blue" compound

Fig. 3. Dependence of the optical density of solutions of the "blue" compound on the concentration of rhenium. a –Re : Sn = 1 : 1; b –in the absence of $SnCl_2$

Figure 2: Fig. 3. Dependence of the optical density of solutions of the "blue" compound on the concentration of rhenium. a –Re : Sn = 1 : 1; b –in the absence of $SnCl_2$

on the concentration of rhenium.
a –Re : Sn = 1 : 1; *b* –in the absence of $SnCl_2$.

The molar extinction coefficient is 53 for the specific conditions: 8 *N* HCl and a thiourea concentration of 0.2 mol/l. All the compounds described have been isolated in crystalline form; their composition is being studied.

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Note: Figure translations are in progress. See original paper for figures.