
**POTENTIOMETRIC AND THERMODYNAMIC INVESTIGATION OF
RHENIUM(V) COMPLEXES WITH 1-METHYL-2-
MERCAPTOIMIDAZOLE**

G. A. GOUDA, M. R. SHATAT, T. A. SEAF ELNASR AND M. H. ABDALLAH

Faculty of Science, Al-Azhar University, Assiut, 71524, Egypt

Corresponding author. E-mail: ggouda1973@yahoo.com

Abstract

Stability constants of 1-methyl-2-mercaptoimidazole with rhenium(V) were determined potentiometrically in acidic medium (4 M HCl) at different temperatures. The dissociation constants pK of 1-methyl-2-mercaptoimidazole as well as the stability constants ($\log K$) of their complexes were determined at varieties temperatures. The corresponding thermodynamic parameters (ΔG° , ΔH° and ΔS°) were determined and discussed. The formation of the metal complexes has been found to be exothermic.

Key words: Potentiometric, rhenium(V), formation constants, thermodynamics.

Characteristic stability constants may be important for predicting various chemical processes, such as isolation, extraction and concentration methods,^[1,2] since many elements are present in trace amounts, and can be separated by complexation reagents. Bejerrum's^[3] dissertation being initiative in developing this field. Metal complexation not only brings the reacting molecules together to give activated complex^[4] but also polarized electrons from the ligands towards the metal. The relation between stability and basicity of the ligands is indicated by the formation constant and free energy change values. The stability constant dependent on several factors such as: electronegativity, hardness or softness of the donor atoms on the ligand, the metal ion, nature of the ligand, the ionic radius and charge of the oxidation state on the metal core respectively. One available method is the potentiometric titration using ligand redox electrodes based on sulfur compounds and their oxidized forms. Many workers^[5-18] have reported their results on metal-ligand stability constants and their oxidized forms.

Experimental

To determine the formation constants of rhenium(V)-1-methyl-2-mercaptoimidazole in 4 M HCl at different temperatures a potentiometric method of employed. Equilibrium concentrations of 1-methyl-2-mercaptoimidazole are calculated by the following equation:

$$\lg[L] = \frac{E_{\text{initial}} - E_i}{1.9837 \cdot 10^{-4} T} + \lg C_L^{\text{initial}} + \frac{1}{2} \lg \frac{V_{\text{initial}}}{V_{\text{all}}}$$

where E_{initial} - initial equilibrium potential of the oxidation-reduction system in the absence of rhenium(V); E_i - equilibrium potential at end point of titration. C_L^{initial} -

initial analytical concentration of 1-methyl-2-mercaptoimidazole; $V_{\text{initial}}/V_{\text{all}}$ - the ratio of the initial volume to the total volume of the system; T - the temperature of the experiment in Kelvin degree. Determined at each point of the titration equilibrium concentration of the ligand. The function \bar{n} was calculated at each titration by the formula:

$$\bar{n} = \frac{C_L - [L]}{C_{\text{Re(V)}}}$$

where \bar{n} is the average degree of formation derived from the titration curves of a ligand with metals; C_L is the concentration of 1-methyl-2-mercaptoimidazole; $[L]$ - equilibrium concentration of 1-methyl-2-mercaptoimidazole; $C_{\text{Re(V)}}$ - the concentration of rhenium(V). All the calculations are employed using a computer «Intel® Core™ i7».

Results and Discussion

Among the ligand redox electrodes used for the study of complexes represent an important type on the basis of sulfur-containing organic compounds and their oxidized forms. The preparation of such electrodes is based on the reversible oxidation of thione or thiol-containing compounds to the corresponding disulfides.

The complexation process of rhenium(V) with 1-methyl-2-mercaptoimidazole proceeds stepwise and reversible. It is natural that the stability of these complexes depends on the nature of the substituent in the 1-methyl-2-mercaptoimidazole.

The addition of $\text{H}_2[\text{ReOCl}_5]$ to a solution (0.0759 M) containing 1-methyl-2-mercaptoimidazole (0.0259 M) and its oxidized form in the acid medium (4 M HCl) causes a change in color of solution to red, with increasing concentration of $\text{H}_2[\text{ReOCl}_5]$ the solution is changed to purple, blue and finally to green. The adding, to the green solution 1-methyl-2-mercaptoimidazole color change of the solution is reversed. This fact indicates the gradation and reversibility of the complexation of rhenium(V) with 1-methyl-2-mercaptoimidazole. In the titration of rhenium(V)-1-methyl-2-mercaptoimidazole system and its oxidized form, an increase in the magnitude of the equilibrium potential, indicating a other participation in complexation of rhenium(V) with 1-methyl-2-mercaptoimidazole than its oxidized form. At each point, equilibrium is established within 5-10 minutes. By potentiometric titration each values of the equilibrium concentration of 1-methyl-2-mercaptoimidazole and E are determined. Using values of $[L]$ and taking together with both the analytical concentrations of $\text{H}_2[\text{ReOCl}_5]$ and 1-methyl-2-mercaptoimidazole formation constants can be calculated. Some data determined by potentiometric titration of rhenium(V) with 1-methyl-2-mercaptoimidazole in 4 M HCl at 273 °K, are presented in Table 1.

Table 1. Data obtained by potentiometric titration of rhenium(V) with 1-methyl-2-mercaptoimidazole in 4 M HCl at 273 °K

$C_{Re(V)} \cdot 10^3$	$C_L \cdot 10^2$	$\Delta E, mV$	$-\log [L]$	\bar{n}
<i>Mole/l</i>				
4.536	2.323	61.54	2.745	4.726
4.773	2.309	74.54	2.986	4.621
5.240	2.281	108.98	3.624	4.308
5.808	2.247	155.54	4.487	3.864
6.358	2.214	178.98	4.923	3.481
6.892	2.182	185.21	5.041	3.165
7.413	2.151	188.32	5.101	2.901
7.917	2.121	193.21	5.195	2.678
8.409	2.092	196.47	5.258	2.487
8.886	2.063	199.14	5.310	2.321
9.351	2.035	201.44	5.355	2.176
10.245	1.982	203.35	5.396	1.934
11.092	1.931	207.24	5.474	1.741
12.664	1.837	215.57	5.638	1.451
14.089	1.752	220.54	5.740	1.243
14.754	1.712	225.32	5.834	1.160
15.996	1.638	228.62	5.904	1.024
17.135	1.570	230.87	5.955	0.916
18.184	1.508	233.36	6.010	0.829
19.608	1.422	236.56	6.081	0.725
20.881	1.346	238.47	6.128	0.644
22.024	1.278	240.21	6.172	0.580
23.692	1.178	244.55	6.270	0.497
25.118	1.093	246.08	6.314	0.435

Figure (1) showed potentiometric titration formation curves of rhenium(V)-1-methyl-2-mercaptoimidazole complexes at different temperature in 4 M HCl.

Potentiometric titration curves showed that rhenium(V)-1-methyl-2-mercaptoimidazole system in presence of 4 M HCl at different temperatures consistently produced four types of complexes. The $\log K_i$ values of rhenium(V) with 1-methyl-2-mercaptoimidazole from the titration curves by Bjerrum method at half-integer values ^[19-20] of the degree of formation (\bar{n}) is presented in Table 2.

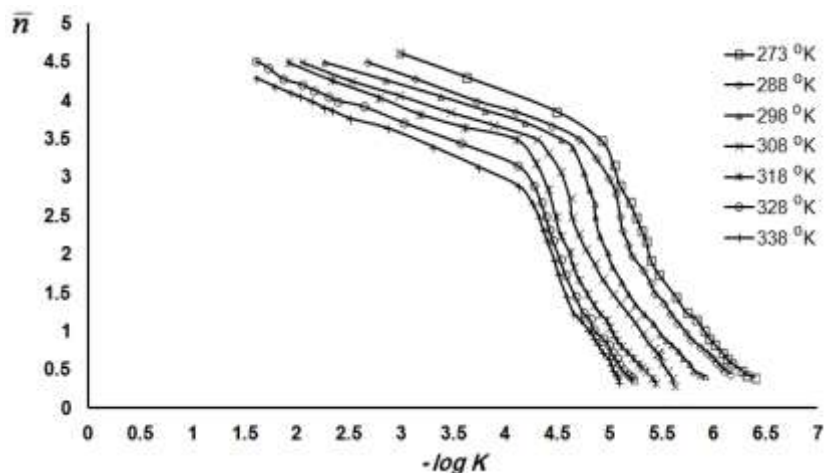


Fig. 1. Plots of \bar{n} against $(-\log K)$ for rhenium(V) with 1-methyl-2-mercaptoimidazole complexes in 4 M HCl at different temperatures.

Table 2. Formation constant values of rhenium(V)-1-methyl-2-mercaptoimidazole in 4 M HCl at different temperatures

T, °K	$[\text{ReOLCl}_4]^-$	$[\text{ReOL}_2\text{Cl}_3]$	$[\text{ReOL}_3\text{Cl}_2]^+$	$[\text{ReOL}_4\text{Cl}]^{2+}$
	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$
273	6.27	5.61	5.26	4.92
288	6.10	5.43	5.10	4.71
298	5.81	5.17	4.86	4.53
308	5.55	5.03	4.64	4.31
318	5.31	4.78	4.48	4.10
328	5.13	4.65	4.39	3.45
338	5.02	4.57	4.32	3.11

These data show that with increasing amount coordinated molecules 1-methyl-2-mercaptoimidazole $\log K_i$ decreases. Stepwise formation constant ratios were as follows: $K_1/K_2 = 4.57$; $K_2/K_3 = 2.24$; $K_3/K_4 = 2.19$ at 273 °K. These data indicate that the ratio stepwise formation constants are not so large enough, so it was necessary to clarify the estimated constants either successive approximation method or by the "pH-meter" program [21]. However, attempts to refine the estimated formation constants were not sufficient.

The equilibrium constant (K) varies with temperature according to the Van't Hoff [22-23] equation:

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$$

R is the universal gas constant, T is the absolute temperature (in $^{\circ}\text{K}$) and ΔH° is the enthalpy change. To obtain the integrated equation, it is convenient to first rewrite the Van't Hoff equation as

$$\frac{d \ln K}{d \frac{1}{T}} = - \frac{\Delta H^{\circ}}{R}$$

Thus, for exothermic reactions, the ΔH° is negative and K decreases with temperature, but for endothermic reactions ΔH° is positive and K increases with temperature. In accordance with the data [24] values of stability constants after verifying these methods vary slightly. In this regard, the stability constant of rhenium(V)-1-methyl-2-mercaptoimidazole complexes, some of the potentiometric titration curves, were used to estimate the thermodynamic properties of the complexation by the temperature coefficient. The ΔH° values were determined from the slope of the straight line obtained by plotting $\log K_i$ against $1/T$ (Fig. 2). The change in entropy is determined by the interval intercepts on the y-axis, these lines ($\Delta S^{\circ} = R * \text{interception}$) [25,26]. Gibbs energy [27] was calculated from the equation $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ (Table 3). Calculated thermodynamic function showed that the isobaric-isothermal capacity becomes less negative with increasing number of coordinated molecules of 1-methyl-2-mercaptoimidazole. This experimental finding may be due to an increase in the steric hindrance that prevent in entering molecules of 1-methyl-2-mercaptoimidazole to center the inner sphere complexes [28].

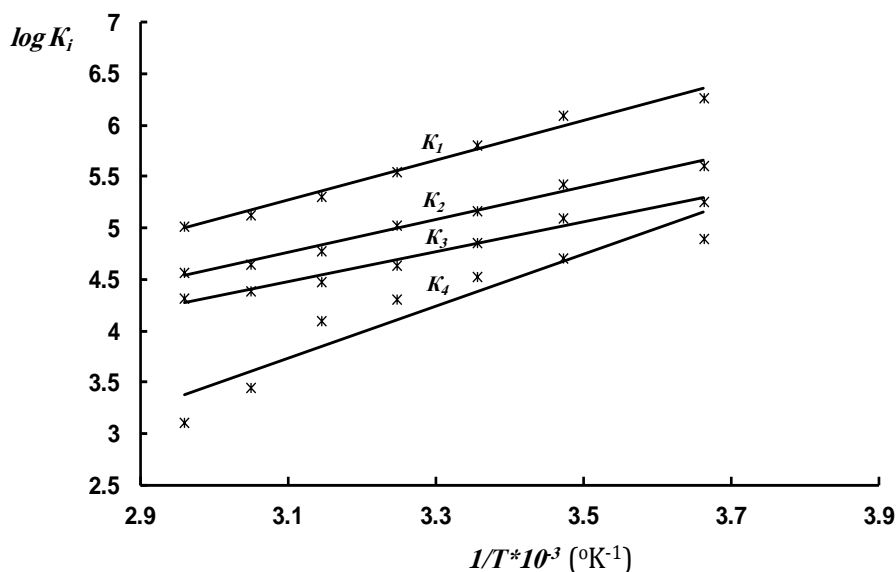


Fig. 2. Plots of $\log K_i$ against $1/T$ for rhenium(V)-1-methyl-2-mercaptoimidazole complexes in 4 M HCl at different temperatures.

Table 3. The thermodynamic parameters of the formation rhenium(V)-1-methyl-2-mercaptoimidazole complexes in 4 M HCl at different temperatures

Species	$-\Delta H^\circ$, kJ/mole	$-\Delta G^\circ$, kJ/mole	$-\Delta S^\circ$, J/mole·K
$[\text{ReOLCl}_4]^-$	36.97	32.88	13.70
$[\text{ReOL}_2\text{Cl}_3]$	22.36	28.97	3.05
$[\text{ReOL}_3\text{Cl}_2]^+$	27.84	27.65	0.65
$[\text{ReOL}_4\text{Cl}]^{2+}$	48.78	24.99	79.86

The values of the entropy changes for the mono-substituted complex compared to the disubstituted complex has a much greater significance ^[29]. Thus, as the higher value of ΔS° can be interpreted in favor substitution of chloride ion in the transposition to the oxygen oxorhenium groups is apparently due to the fact that Re-Cl distance being in trans-position to the oxygen of the oxorhenium group in the equatorial plane ^[30]. Significant decrease of ΔS° is probably due to the fact that the introduction of a second molecule of 1-methyl-2-mercaptoimidazole in the inner coordination sphere becomes more difficult and that such molecule may replace one of the four chloride ions that are in the equatorial plane ^[31].

Mole fractions are commonly used to calculate the concentrations of the individual complexes on the basis of the formation constants. Mole fractions of a particular form of the complex compressed as ratio of the concentration of the complex to the total concentration of the metal ion ($[ML_i]/[\text{Metal ion}] = X_i$). To determine the field dominance of a complex in the form of rhenium(V)-1-methyl-2-mercaptoimidazole in 4 M HCl was calculated from the distribution curves at different temperatures. Figure 3 shows the distribution curves of complex models at 328 °K.

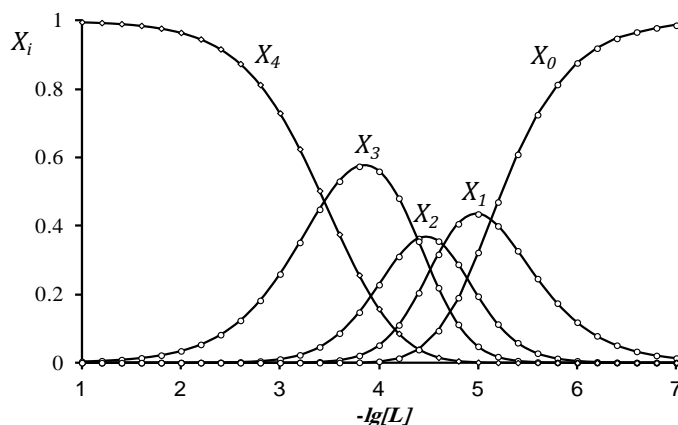


Fig. 3. Distribution curves of rhenium(V)-1-methyl-2-mercaptoimidazole complexes at 328°K; where $X_0 = [\text{ReOCl}_5]^{2-}$, $X_1 = [\text{ReOLCl}_4]$, $X_2 = [\text{ReOL}_2\text{Cl}_3]$, $X_3 = [\text{ReOL}_3\text{Cl}_2]^+$, $X_4 = [\text{ReOL}_4\text{Cl}]^{2+}$.

Analysis of the distribution curves show that increasing temperature has little effect on the proportions of the maximum output value for all complexes. Increasing temperature causes X_i^{max} being shifted towards higher values of equilibrium concentration of 1-methyl-2-mercaptoimidazole (Table 4).

Table 4. The X_i^{max} output equilibrium values for rhenium(V)-1-methyl-2-mercaptoimidazole complexes in 4 M HCl at different temperatures

Species	Values $-lg [L]$ at X_i^{max}						
	273 °K	288 °K	298 °K	308 °K	318 °K	328 °K	338 °K
$[ReOLCl_4]^-$	6.0	5.8	5.6	5.4	5.2	5.0	4.8
$[ReOL_2Cl_3]$	5.4	5.2	5.0	4.8	4.6	4.4	4.4
$[ReOL_3Cl_2]^+$	5.0	4.8	4.6	4.4	4.2	3.8	3.6

Based on these data it is possible to choose the optimum conditions for the isolation of certain complex, establishing their composition and structure.

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