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MECHANISM OF COMPLEX FORMATION BETWEEN $[\text{AuCl}_4]^-$ AND L-METHIONINE

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Abstract

The kinetics of the reaction between tetrachloroaurate(III) ion and L-methionine has been studied spectrophotometrically by using stopped-flow technique in 0.1 M HClO_4 as the function of temperature. The fast reaction was ascribed to the formation of short living square-planar $[\text{AuCl}_2\text{Met}]^+$ complex ion, that was reduced in the slower reaction step. The activation parameters (ΔH^\ddagger and ΔS^\ddagger) for complex formation were determined. The entropy of activation was compatible with an associative reaction mechanism.

Introduction

L-methionine (L-Met) belongs to the naturally occurring amino acids containing thiol group. It forms chelates with many metal ions mostly by coordinative binding to amino- and carboxyl groups of α -amino acid residue [1]. This work deals with the investigation of the equilibrium and kinetics of complex formation between $[\text{AuCl}_4]^-$ and L-Met. Since Au(III) is isoelectronic to Pt(II), this reaction is an excellent model system for the elucidation of the reaction mechanism between biomolecules and Pt(II) complexes that exert anticancer activity.

Experimental

1×10^{-2} M stock solutions of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and L-methionine were prepared in 0.1 M HClO_4 shortly before use (all used chemicals were p.a. quality). The absorption spectra were recorded using Perkin Elmer Lambda 35 spectrophotometer. Kinetic measurements were performed using HI-TECH stopped-flow equipment in the temperature range from 282 to 303 K.

Results and Discussion

The absorption spectra of solutions containing 1×10^{-5} M $[\text{AuCl}_4]^-$ and 5×10^{-5} M L-Met were followed in 0.1 M HClO_4 as the dependence of time. The spectral changes indicated two processes, according to the relations:

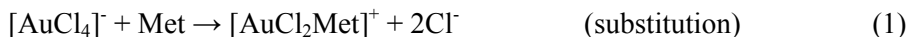


Fig.1 represents the changes of the absorption spectra in the fast reaction step, which were followed by two well defined isobestic points. These spectral changes were ascribed to the substitution reaction due to the formation of $[\text{AuCl}_2\text{Met}]^+$

complex ion according Eq.1, with the shoulder around 280 nm. The second process (Eq. 2), followed by the disappearing of the absorption spectra, was considered to be the reduction of $[\text{AuCl}_2\text{Met}]^+$ complex ion. The change of the absorbance vs. time at 280 nm is presented in Fig.1 (inset).

The stoichiometry of the reaction (1) was confirmed by the molar ratio and Jobb's methods [2], using the absorbance at the maximum of the kinetic curves as the measure of concentration of complex ion.

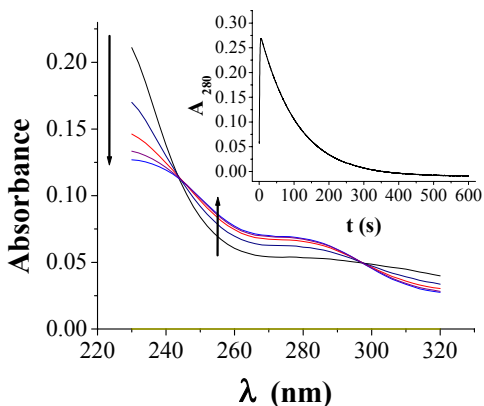


Fig. 1. Time dependence of absorption spectra of solution containing 1×10^{-5} M $[\text{AuCl}_4]^-$ and 5×10^{-5} M L-Met at pH 1. Inset: kinetic curve at 280 nm

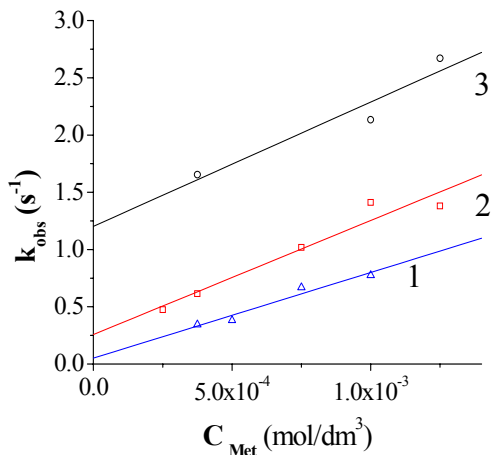


Fig. 2. Experimental rate constants (k_{obs}) as a function of L-Met concentration at pH 1 and 282 K (1); 294 K (2); 303 K (3).

The kinetic of the reaction between $[\text{AuCl}_4]^-$ and L-Met was investigated at pH 1 under the pseudo first order conditions as the function of temperature, keeping the concentration of Au(III) complex ion constant (5×10^{-5} M) and varying [L-Met] from 2×10^{-5} M to 1×10^{-3} M. The kinetic curves in the fast reaction step were fitted to the function $(A_f - A)/(A - A_o) = \exp(-k_{\text{obs}}t)$ (A_o and A_f were the initial and final (on the plateau of A vs. t curve) absorbancies, respectively). The typical dependence of k_{obs} vs. [L-Met] for the substitution reactions of square planar complexes was obtained in the fast reaction step:

$$k_{\text{obs}} = k_I + k_{II} [\text{L}_f] \quad (3)$$

where k_{obs} represents the observed pseudo first order rate constant, k_I is the solvent dependent rate constant and k_{II} is the second order rate constant which is characteristic for direct nucleophile attack. The linear plots of k_{obs} vs. [L-Met] were obtained in all cases and are presented on Fig.2. k_I and k_{II} were determined from the intercept and the slope of the plots, and are given in Table 1. The dependence of k_{II} on temperature allowed the calculations of the activation parameters of complex formation (Eq. 4).

$$k_{II} = kT/h \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT) \quad (4)$$

The values of enthalpy ($\Delta H^\ddagger = 9.9$ kJ/mol) and entropy ($\Delta S^\ddagger = -154.3$ J/mol K) were obtained using Eyring's equation.

Table 1. Values of rate constants k_I and k_{II} obtained from linear plots k_{obs} vs. L-Met concentration

T(K)	$10^2 \times k_{II}(\text{M}^{-1}\text{s}^{-1})$	$k_I(\text{s}^{-1})$
282	7.48	0.051 ± 0.001
294	9.17	0.257 ± 0.001
303	10.86	1.202 ± 0.001

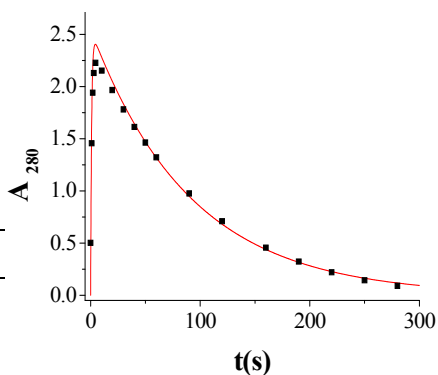


Fig. 3. Dependence of absorbance at 280 nm on time; solid curve calculated according Eq.(5); points - experimental results

The experimental kinetic curves at 280 nm (Fig. 1, inset) are typical for two consecutive reactions [3]. The dependence of absorbance on time can be presented as:

$$A = \frac{k_1}{k_2 - k_1} A_\infty (e^{-k_1 t} - e^{-k_2 t}) \quad (5)$$

where k_1 and k_2 are pseudo first order rate constants for reactions (1) and (2), respectively, and $[A]_\infty$ is the absorbance on the plateau of A vs. t curve. Using Eq. 5, the rate constants $k_1 = 1.06 \text{ s}^{-1}$ and $k_2 = 0.01 \text{ s}^{-1}$ for the solution containing $[\text{AuCl}_4]^- = 2.5 \times 10^{-5} \text{ M}$ and $[\text{Met}] = 10^{-4} \text{ M}$ were obtained. Using these values the dependence of absorbance at 280 nm (A_{280}) vs. t was recalculated and presented on Fig. 3 as solid line, since the points represent the experimental results. As can be seen, the calculated results are in good agreement with the experimental data. These finding supports the proposed reaction model.

Conclusion

The reaction between $[\text{AuCl}_4]^-$ and L-methionine involves ligand substitution followed by the reduction of the formed complex ion. The large negative value of the entropy indicated an associative mode of activation (I_a or A mechanism) in the first reaction step. This finding indicates that bond-making with the entering ligand is important in the activation processes and that the leaving group is still tightly bound to the metal center in the transition state. The effect of ligand on the reduction step is under the investigation.

References

- [1] E. Raux, H. K. Leech, R. Beck..., *Biochem. J.*, 2003, **370**, 505-516.
- [2] J. Luthern, A. Peredes, *Journal of Materials Science Letters*, 2000, **19**, 185-188.
- [3] R. Schmidt, V. N. Sapunov, *Non-formal kinetics*, Verlag Chemie, Basel, 1982.