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and Applied Aspects of Physical Chemistry*

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SPECTROPHOTOMETRIC AND UPLC STUDY OF REACTION BETWEEN $[\text{AuCl}_4]^-$ AND QUERCETIN

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Abstract

The equilibrium and kinetics of the reaction between tetrachloroaurate(III) ion (AuCl_4^-) and quercetin in 0.1 M HClO_4 were studied spectrophotometrically. The fast and the slow reaction steps were distinguished in the reaction mechanism, depending on the ratio of AuCl_4^- and quercetin concentration. The stoichiometry of reaction, determined by molar ratio and Jobb's methods, was 1:1. The kinetics of complex formation was followed under the pseudo-first order conditions by measuring the absorbance at 294 nm vs. time as the function of quercetin concentration in 5 – 15 fold excess.

Introduction

The interaction of flavonoids with metal ions may change the antioxidant activity and biological effects of flavonoids [1]. Quercetin (Q) is of a great importance for the potential biological and clinical use, because it is a potent inhibitor of some enzymes (myeloperoxidase, reductase) and has the antioxidant properties due to free radical scavenging. Au(III) is a strong oxidizing agent and is, therefore, highly toxic. One of the most investigated complexes of Au(III) with halogens is the tetrachloroaurate ion. The reaction between Au(III) and different flavonoids as the analytical method for the determination of gold in cosmetic preparates was investigated previously [2]. The aim of this work was to investigate the reaction between Q and $[\text{AuCl}_4]^-$.

Experimental

All chemicals were of reagent grade quality. Absorption spectra and kinetic experiments were performed on the Perkin Elmer Lambda 35 UV-Vis spectrophotometer fitted to the universal rapid kinetic accessory HI-TECH model SFA 12. The chromatographic experiments were performed on Waters ACQUITY Ultra Performance Liquid Chromatography (UPLC) system, using an ACQUITY UPLCTM BEH C_{18} , 1.7 μm , 50mm \times 2.1mm column as a stationary phase. The mobile phase was composed of 0.5 vol % H_3PO_4 in water (A) and acetonitrile (B) (A:B=70:30) at a constant flow rate of 0.4 mL/min.

Results and Discussion

Absorption spectra and chromatograms

The reaction between $[\text{AuCl}_4]^-$ and Q was studied spectrophotometrically in 0.05M HClO_4 1:1 water/methanol solution. The absorption spectra of solution containing equimolar concentrations of Q and $[\text{AuCl}_4]^-$ (2.5×10^{-6} M) in 0.05M HClO_4 as the function of time are presented in Fig. 1A. Quercetin has the absorption spectra with the maxima at 250 and 370 nm. The decrease of the intensity of these bands and the simultaneous rising of the absorption band at 294 nm indicates the formation of the typical oxidation product due to the Q oxidation by Au(III). The spectral

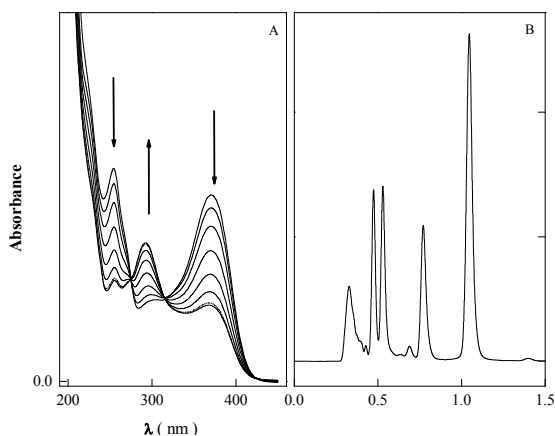


Fig. 1. Time dependence of A) absorption spectra of 2.5×10^{-6} M Q and $[\text{AuCl}_4]^-$ in 0.05M HClO_4 1:1 water/methanol solution; B) chromatogram of the same solution obtained at 294 nm (injection volume 10 μL).

changes were followed by two quite well defined isobestic points at 273 and 323 nm. The reaction was almost completed after 35 min under the given experimental conditions.

The analysis of chromatogram (Fig.1 B) indicates clearly, that at least three oxidation products and neutral quercetin form are detectable in solution. These products were identified according the literature data [3] and are given in Table 1. They resulted from solvent addition (methanol or/and water) to p-quinonemethide, formed by two-electron oxidation of Q [3].

Kinetic studies

It is reasonable to assume that oxidation of Q proceeded as the consequence of the formation of the short time living intermediate formed between $[\text{AuCl}_4]^-$ ion and Q. The absorption band with low molar absorptivity, in the wavelength range from 400 to 550 nm (data not shown) can be ascribed to the short living complex between $[\text{AuCl}_4]^-$ and Q.

Table 1. Spectrophotometric and UPLC data for Q, $[\text{AuCl}_4]^-$ and their reaction products in 0.05M HClO_4 1:1 water/methanol solution

species	t_r (s)	λ_{max} (nm)
QH_2O	28.3	294
QH_2OMeOH	31.6	294
QMeOH	45.7	294
QH_2	61.6	254, 370
$[\text{AuCl}_4]^-$	213.2	225, 315

The complex formation was followed at 450 nm, in the excess of Q, under the pseudo first order conditions. The concentration of $[\text{AuCl}_4]^-$ was 2.5×10^{-6} M, since Q concentration was between 1.25×10^{-5} M and 5×10^{-5} M. The rise and fall of the absorbance at 450 nm as a function of time (Fig. 2) is characteristic for a reaction

(1) that involves an intermediate C in the overall process during which Q and AuCl_4^- react to give the oxidation product, QX:



QX represents all possible reaction products obtained due to the oxidation of quercetin [3] and C represents the complex between $[\text{AuCl}_4^-]$ and quercetin. The dependence of concentration on time can be presented as:

$$[c] = \frac{k_1}{k_2 - k_1} [c]_\infty (e^{-k_1 t} - e^{-k_2 t}) \quad (2)$$

where k_1 and k_2 are pseudo first order rate constants for complex formation and oxidation process, respectively, and $[c]_\infty$ is the concentration on the plateau of c vs. t curve. Using Eq. 2, the rate constants $k_1 = 0.030 \text{ s}^{-1}$ and $k_2 = 0.002 \text{ s}^{-1}$ for the solution containing $[\text{AuCl}_4^-] = 2.5 \times 10^{-6} \text{ M}$ and $[\text{Q}] = 1.25 \times 10^{-5} \text{ M}$ were obtained. The recalculated results by using these constants are in good agreement with the experimental data. These finding supports the proposed reaction model.

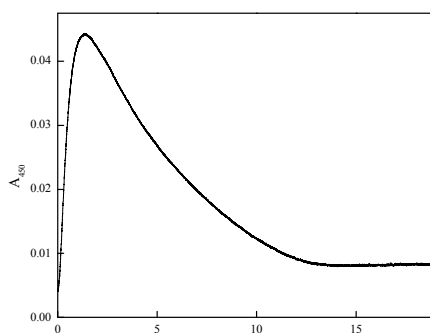


Fig. 2. Kinetic curve for formation of complex between Q and $[\text{AuCl}_4^-]$ recorded at 450 nm ($C_Q = 1.25 \times 10^{-5} \text{ M}$; $C_{\text{AuCl}_4^-} = 2.5 \times 10^{-6} \text{ M}$)

Conclusions

The reaction between quercetin and $[\text{AuCl}_4^-]$ in 0.05M HClO_4 1:1 water/methanol solution leads to the oxidation of quercetin, which resulted in the formation at least three oxidation products. The proposed reaction mechanism involves the complex formation between Q and $[\text{AuCl}_4^-]$. For investigation conditions kinetics of reaction between Q and $[\text{AuCl}_4^-]$ was followed under the pseudo-first order consecutive reaction.

Acknowledgements

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