摘要

Part I. L-抗壞血酸還原$Fe(CN)_5L^{2-}$錯合物之反應動力學探討

維他命 C 還原 $Fe(CN)_5L^{2-}$ (L=pyridine, isonicotinamide, 4,4'-bipyridine, CN^-)錯合物的反應在pH=1-8.0的動力學探討，顯示維他命C反應屬兩電子還原(eq.1)。

$$2Fe(CN)_5L^{2-} + H_2A \rightarrow 2Fe(CN)_5L^{3-} + A + 2H^+ \qquad (1)$$

反應速率決定步驟為第一個電子的還原。維他命 C 依不同 pH 值溶液以 H_2A、HA^-、和 A^{2-}形式呈現，分別為 k_0、k_1、k_2，每種型態皆具有反應活性，且由於反應速率隨 pH 值增加而變快，反應活性顯然為 $A^{2-}>HA^->H_2A$。當 L = py, isn, bpy 和 CN^-時，在 μ = 0.10M ($HClO_4/LiClO_4$)，T＝25℃條件下，反應速率常數分別得 k_0 = 1.8 ± 0.1, 7.0 ± 0.3, 4.4 ± 0.3 和 0.4 ± 0.1 $M^{-1}s^{-1}$; $k_1 = (2.4\pm0.2)\times10^3$, $(5.7\pm0.2)\times10^3$, $(5.3\pm0.1)\times10^3$ 和 $(6.4\pm0.1)\times10^2$ $M^{-1}s^{-1}$; $k_2 = (6.5\pm0.1)\times10^8$, $(8.8\pm0.1)\times10^8$, $(7.9\pm0.1)\times10^8$ 和 $(3.6\pm0.1)\times10^7$ $M^{-1}s^{-1}$。動力學結果與 Marcus 預測值相符，顯示此氧化還原反應屬外圈電子轉移機構。

Part II. Al(III)與 quercetin 及類黃酮衍生物形成螯合錯合物光譜及動力學探討

在 CH_3OH/H_2O (9:1)的酸性溶液下 Al(III)與 quercetin、fisetin、luteolin、5-hydroxyflavone 和 3-hydroxyflavone 的形成錯合物進行探討，由光學計量結果顯示，所有類黃酮與 Al(III)形成的錯合物皆為 1：1 的形態，由元素分析與質譜結果，Al(III)與類黃酮的螯合屬於四配位鍵結。比較 fisetin、luteolin、5HF 和 3HF 螯合錯合物的 ^{1}H-NMR 的光譜結果，顯示 Al(III)與 quercetin 錯合物是兩個異構物所組成，分別螯合在 O3、O4 和 O4、O5 位置。比較單一螯合位置的類黃酮錯合物，其平衡常數與形成反應速率皆相似，表示 quercetin 螯合在 O3、O4 位置或 O4、O5 位置的螯合動力學與熱力學穩定性皆相似。

Part III. Quercetin、rutin 和 taxifolin 在鹼性條件與 O_2 之反應探討

在絕氧條件下，quercetin 在 0.01M NaOH 溶液中相當穩定，但當曝露在空氣中時，則會迅速氧化形成 quinone 產物，而 rutin 和 taxifolin 溶液只有在飽和氧氣下才會氧化，且非常的緩慢。類黃酮於 0.01M NaOH 溶液中，μ=0.1M $LiClO_4$，且在飽和氧條件下測得 quercetin、rutin 及 taxifolin 的氧化速率分別為 $(4.50\pm0.09)\times10^{1}$ (Quercetin)、$(6.64\pm0.09)\times10^{-2}$ (rutin)及$(3.09\pm0.09)\times10^{-3}$ (taxifolin) $M^{-1}s^{-1}$。Quercetin 的反應速率大了 2 次冪，主要是由於 C_3 上的羥基去氫化和 pyrone 與 catechol 之間的共振效應有關。

Part IV. 兒茶酚及類黃酮在甲醇溶劑中與 dpph·之氧化還原反應

本文主要探討於甲醇中 dpph·與一系列 catechol 的反應性，反應經由兩個電子的氧化形成 quinone 產物，動力學結果確定 catechol 反應速率決定步驟為第一個電子氧化，當第一個電子氧化後，形成 semiquinone radical，隨即與另一個 dpph·迅速反應形成最後產物 quinone。於甲醇溶液下，μ＝0.10M $[(n\text{-}Bu)_4N]ClO_4$，依取代基的不同，所測得的氧化速率 k_{ox} 介於 10^{1}-10^{2} $M^{-1}s^{-1}$ 之間。rutin 與 taxifolin 的氧化反應同時也被探討。動力學結果顯示，pyrone 和 catechol 之間的共振效應對 flavonoid 的反應性確實扮演重要的角色。

Abstract

Part I. Kinetic studies of the reactions of pentacyanoferrate(III) complexes with L-ascorbic acid

The reduction of $Fe(CN)_5L^{2-}$ (L=pyridine, isonicotinamide, 4,4'-bipyridine, cyano) complexes by ascorbic acid has been subjected to a detailed kinetic study in the range of pH 1-8.0. The rate law of the reaction is interpreted as a rate determining reaction between Fe(III) complexes and the ascorbic acid in the form of H_2A(k_0), HA^-(k_1) and A^{2-}(k_2), depending on the pH of the solution, followed by a rapid scavenge of the ascorbic acid radicals by Fe(III) complex. With given Ka_1 and Ka_2, the rate constants are k_0=1.8±0.1, 7.0±0.3, 4.4±0.3 and 0.4±0.1 $M^{-1}s^{-1}$, k_1=(2.4±0.2)×10^3, (5.7±0.2)×10^3, (5.3±0.1)×10^3 and (6.4±0.1)×10^2 $M^{-1}s^{-1}$, k_2=(6.5±0.1)×10^8, (8.8±0.1)×10^8, (7.9±0.1)×10^8 and (3.6±0.1)×10^7 $M^{-1}s^{-1}$ for L=py, isn, bpy and CN^-, respectively, at μ=0.10M $HClO_4/LiClO_4$, T=25℃. The kinetic results are compatible with the Marcus prediction.

Part II. Spectroscopic and kinetic studies of Al(III) complexes of quercetin and related flavonoids

The formation reactions of Al(III) complexes of quercetin, fisetin, luteolin, 3- and 5-hydroxyflavones, were studied in CH_3OH/H_2O (9:1) acidic medium. The spectrophotometric titration of flavonoids with Al(III) showed a 1:1 stoichiometry of for all complexes of flavonoids under study. The elemental analysis and mass spectral results of the quercetin complex further indicated that Al(III) ion formed a four coordinated complex with quercetin. The comparison of ^{1}H-NMR spectra of complexes of fisetin, luteolin, 3- and 5-hydroxyflavones with that of the quercetin complex suggested that two isomers, namely O_3, O_4 and O_4, O_5 chelated complexes, were formed for quercetin. The similarity in affinities and rate constants of the formation of the model complexes further supported that both the kinetic and the thermodynamic stabilities of the quercetin complexes formed by O_3 and O_4 chelation and O_4 and O_5 chelation were comparable with each other.

Part III. Base Catalyzed Autoxidation of Quercetin

The quercetin in 0.01M NaOH solution underwent steady oxidation when it was exposed to air with the formation of the quinone product. For the taxifolin and rutin, the oxidation occurred only when the solutions were saturated with O_2, but very slowly. The specific rate constants of oxidation of the flavonoids in 0.01M NaOH solution at saturated O_2 concentration were measured with the values of $(4.5\pm0.4)\times10^{1}$, $(6.64\pm0.09)\times10^{-2}$ and $(3.09\pm0.09)\times10^{-3}$ $M^{-1}s^{-1}$ for quercetin, rutin and taxifolin, respectively at μ=0.10M $LiClO_4$. The deprotonation of the C_3 hydroxyl group and the conjugation between pyrone and catechol rings account for the reactivity of quercetin toward O_2.

Part IV. Oxidation of Catechols and Flavonoids by dpph·

The reaction of a series of catechols and dpph· has been studied in the methanol solution. The reaction underwent a two electron oxidation with the formation of quinone products. Detailed kinetic study shows that the rate law of the reaction involves the rate determining step of one-electron oxidation of the catechols to form the corresponding semiquinone radicals, followed by the rapid scavenge of the radicals to form the final products. The specific rate constants, measured at $\mu =$ 0.10M $[(n\text{-}Bu)_4N]ClO_4$, fall in the range 10^1-10^2 $M^{-1}s^{-1}$, depending on the substituted group of the catechols. The reaction for the oxidation of rutin and taxifolin also has been carried out and the oxidation went to the catechol ring of the flavonoids. The kinetic results show that the conjugation between pyrone and catechol rings plays an important role in the reactivity of the flavonoids.