Determination of Activation Parameters for the Oxidation of Single Ionic Species of Aminoacids

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الملخص

في هذا البحث تم دراسة حركية التاكسد لخمسة احماض امينية وهي الكلايسين والفالين والليوسين والنورليوسين والالنين بوساطة ايون البرمنكنات في محلول مائي. اظهرت النتائج ان التفاعل يحدث بمسارين، الاول غير محفز والثاني محفز ذاتيا عن طريق ثـاني اوكـسيد المنغنيز الغروي الناتج من المسار الاول للتفاعل. ومن اعتماد سرعة التفاعل علـى درجـة الحرارة تم حساب قيمة ثابت سرعة التفاعل غير المحفز (k_n) وثابت سرعة التفاعل المحفـز (k_c). ومن اعتماد سرعة التفاعل غير المحفز على الاس الهيدروجيني للوسط تم حساب ثابت سرعة التاكسد لكل من الايون المزدوج (k_{HA}) والايون السالب (k_A) للحامض الاميني. ومن اعتماد الثوابت k_{HA} و k_A على درجة الحرارة تمكنـا ولأول مـرة مـن حـساب الـدوال الثيرموداينميكية التنشيطية لاكسدة كل من الايون المزدوج والايون السالب للحامض الاميني. وبعد ذلك نوقشت الدوال الثيرموداينميكية استنادا للميكانيكية المقترحة للتفاعل. واظهـرت ان القيم المحسوبة للايونات المنفردة ادق من القيم المحسوبة اعتمـادا علـى ثوابـت الـسرعة الظاهرية (k_n) للتفاعل غير المحفز.

ABSTRACT

In this work the oxidation of five α-aminoacids (glycine, alanine, valine, leucine and norleucine) by permanganate ion in an aqueous phosphate buffer solution were studied. The results showed that the reaction proceed in two pathways. The first is noncatalyzed and the second is autocatalyzed by the colloidal manganese dioxide resulted from the first pathway. The dependences of the noncatalyzed oxidation reaction on the pH of the medium was utilized in calculation of the rate constant for the oxidation of zwitter ionic (k_{HA}) and anionic (k_A) forms.

On the other hand, from the dependences of k_{HA} and k_A on the temperature, the thermodynamic parameters of activation were calculated for the first time for the oxidation of the two ionic species of aminoacids present in the solution. In view of the proposed mechanism for the oxidation reaction the variation of thermodynamic parameters was discussed, and showed that the thermodynamic parameters obtained for single ionic species are more reliable than the other calculated for oxidation of mixture of two ionic species present in solution.

Introduction

A large number of articles have been published concerning the oxidation of aminoacids by permanganate ion in an aqueous solution[1-8]. A few of them have been focused on the kinetic and mechanism of these oxidation reactions. These studies have shown that these reactions proceed by two pathways one is noncatalyzed and the other is autocatalyzed by the colloidal manganese dioxide resulted from the noncayalyzed pathway of the reaction. The value of the rate constants for noncatalyzed (k_n) and autocatalyzed (k_c) oxidation reaction are in facts is an average values for the oxidation of a mixture of two species zwitter and anionic forms present in the solution. In all above studies there are no attempts has been made for calculation of the rate constants and thermodynamic parameters for the oxidation of single ionic species present in the solution. The present work represent an attempt to estimate the values of the rate constant and the thermodynamic parameters for oxidation of single ionic species (zwitter or anionic forms) present in the reaction mixture. These values are more useful in discussion of the reaction mechanism and dependences only on the nature of the ionic species present in the solution.

Experimental

Materials: The aminoacids and all other chemicals used in this work were purchased either from G.A. Fluka or BDH chemical Ltd.

The kinetic measurements: A buffer solution of K_2HPO_4 and KH_2PO_4 was used to keep the pH of the medium constant and preventing the resulted manganese dioxide from precipitation during the reaction course. The permanganate ion concentration was chosen as a rate monitoring species, which has been followed spectrophotometrically using Shimadzu UV-210 double beam spectrophotometer. The inorganic product (MnO_2) absorbs light in the whole visible spectrum. So that it is necessary to correct the absorbance obtained for the permanganate ion at (526 nm) by measuring the absorbance of the mixture at 418 nm (where only the product absorbs light). After that the concentration of permanganate ion was calculated using the following equation[4,5]:
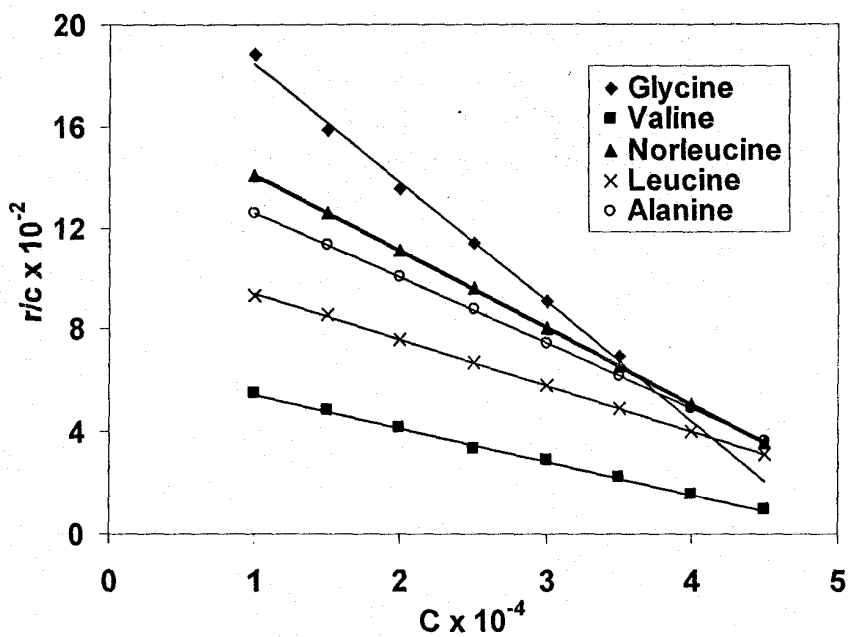
Figure (1): The relation between r/c and c for the oxidation of aminoacids at conc.
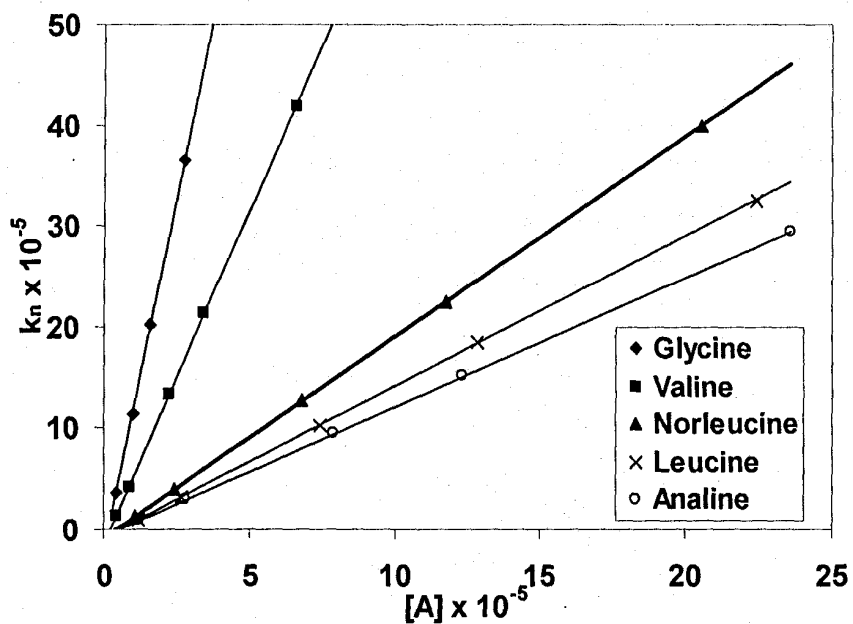0.07 M, pH = 7.5 and temperature = 303 °K

Figure (2): Represent the relationship between k_n and [A] for different
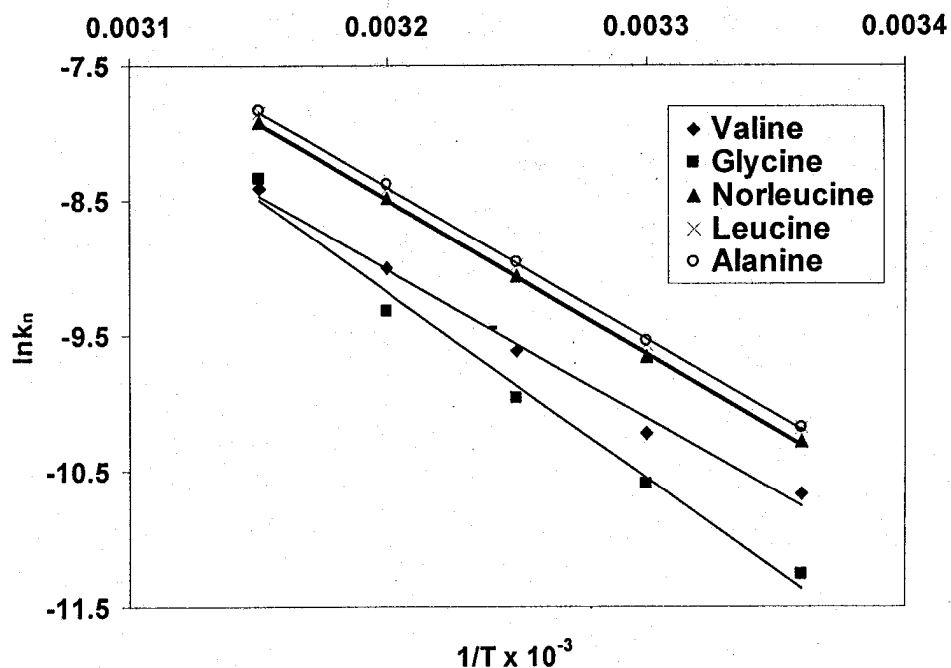aminoacids at temperature

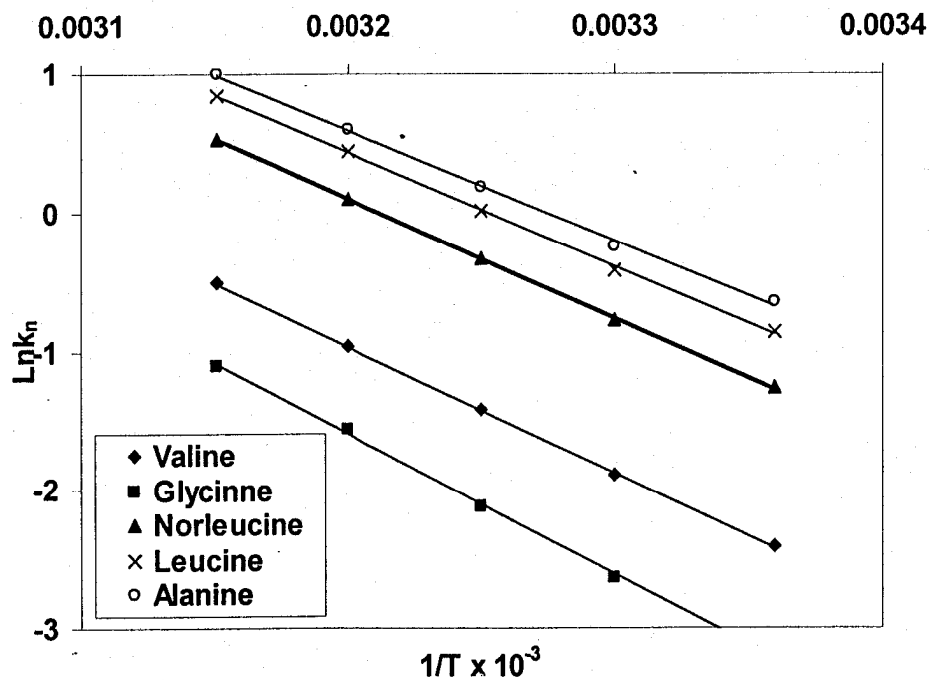**Figure (3): Arrehenius plots for non-catalyzed oxidation reaction of aminoacids**

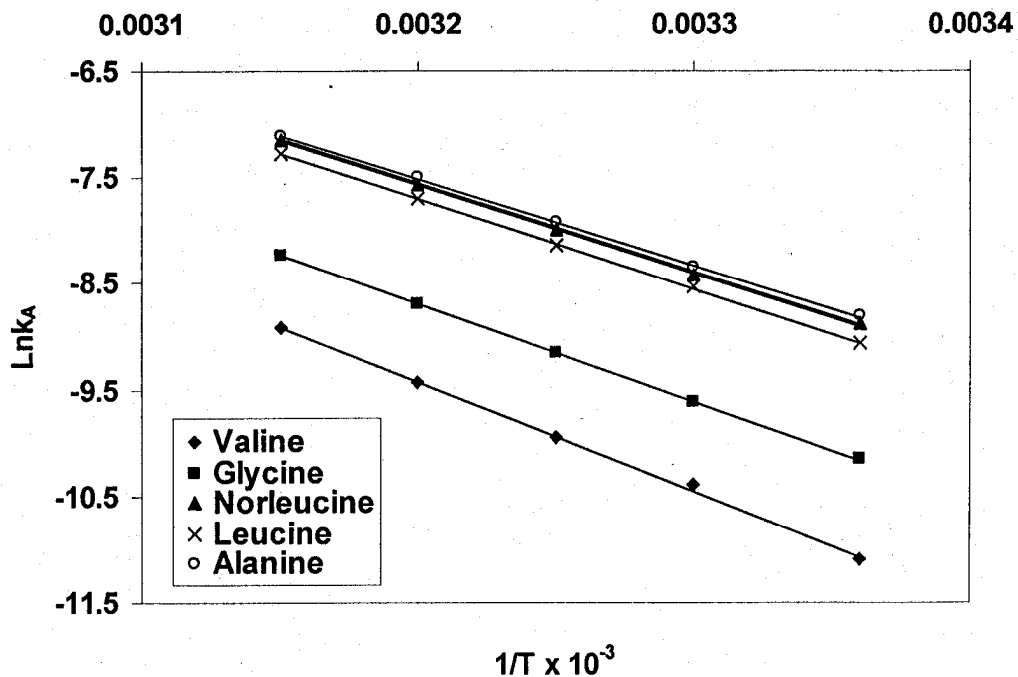**Figure (4): Arrehenius plots for oxidation of zwitter ionic form of aminoacids**

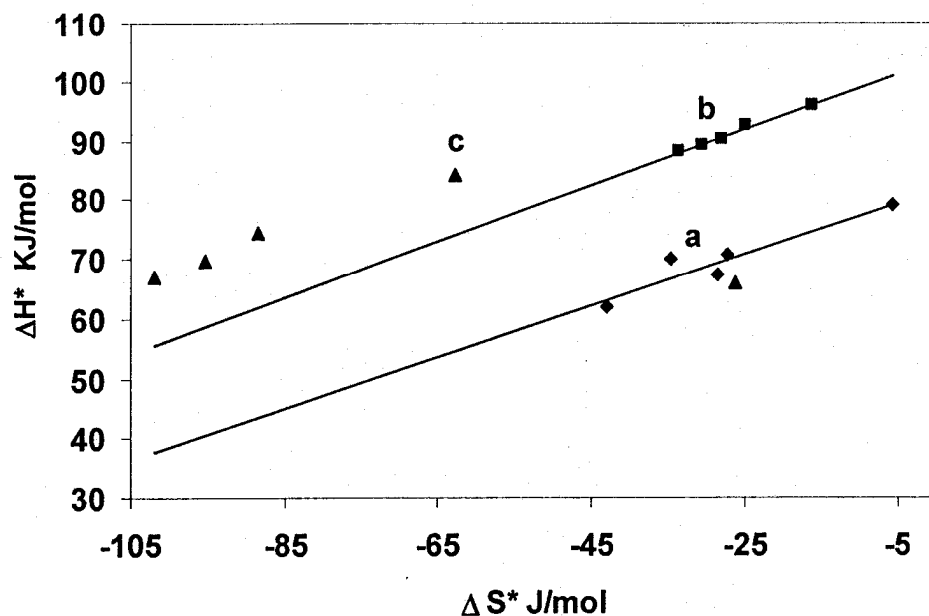Figure (5): Arrehenius plots for oxidation of anionic form of aminoacids

Figure (6): Plots between ΔH^* and ΔS^* for the oxidation of; a: zwitter ionic form; b: anionic form; c: mixed species

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