Kinetics and Mechanism of the Autocatalytic Oxidation of L-Asparagine in a Moderately Concentrated Sulfuric Acid Medium[1]

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Abstract—The reaction kinetics of the Autocatalytic Oxidation of L-asparagine by permanganate ions has been investigated in moderately strong acid medium using the spectrophotometric technique. In all cases studied, an autocatalytic effect due to Mn^{2+} ions formed as a reaction product was observed. Both catalytic and noncatalytic processes were determined to be first order with respect to the permanganate ions while a first and a fractional order with respect to the amino acid for noncatalytic and catalytic reactions were obtained, respectively. The overall rate equation for this process may be written as

$$d[MO_4^-]/dt = k_1'[MnO_4^-] + k_2'[MnO_4^-][Mn^{+2}],$$

where k_1' and k_2' are rate pseudoconstants for noncatalytic and catalytic reactions, respectively. The influence of some factors such as temperature and reactant concentration on the rate constants has been studied, and the activation parameters have been calculated. Reaction mechanisms satisfying observations for both catalytic and noncatalytic routes have been presented.

INTRODUCTION

Due to the biological importance of amino acids, the kinetics and mechanistic study of their oxidation have received considerable attention. The permanganate oxidation process of amino acids in strong acid medium [1–14], neutral and weak basic solution [15–23], and weak acid medium [24–29] have been investigated. The occurrence of an autocatalysis effect in a weak acid medium, neutral aqueous solution, and weak basic medium has been extensive [15–29], whereas no rigorous evidence of such an effect has been reported in a strong acid medium. There have been just two reports [10, 14] of a "double-stage" process vaguely attributed to possible autocatalysis with no thorough information as far as the autocatalysis effect is concerned.

In autocatalytic pathways in which Mn^{2+} ions have been determined responsible for the effect, a mechanism with no free radicals involved has been suggested [28, 29]. In this paper, distinct evidence of an autocatalytic influence of Mn^{2+} for the permanganate oxidation of L-asparagine in a strong acid medium has been presented and a free radical mechanism has been proposed.

In order to avoid any deviation from Beer–Lambert law, contrary to many previous investigations where permanganate absorption has been taken as either higher or in some cases lower than unity, we have determined a larger error for the former case and have obtained more accurate results by setting the absorption near unity at the beginning of the reaction.

EXPERIMENTAL

All the reagents were p.a. Merck or Sigma. The solutions were prepared with tridistilled water deionized and boiled. The permanganate solutions were prepared and tested by the Yogle method [30]. The kinetic progress of the reaction was followed by measuring the absorbance of the permanganate ions at 525 nm with a thermostated (Shimadzu TB-85, ±0.1 K) Shimadzu (2100 Model) UV-VIS spectrophotometer within the temperature range 25–45°C. For the permanganate molar absorption coefficient at 525 nm and in a strong acid solution, a value of 2263 $dm^3/(mol\ cm)$ was obtained.

In all the kinetic measurements, the amino acid was used in an excess amount relative to permanganate.

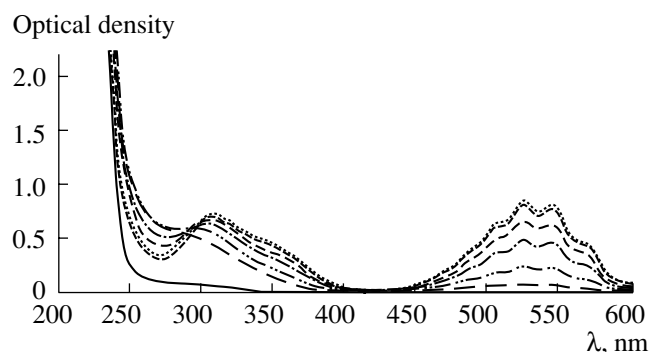[1] This article was submitted by the authors in English.

Optical density

Fig. 1. Spectral changes in the oxidation of asparagine by permanganate ion. $[KMnO_4] = 4 \times 10^{-4}$ mol/dm^3; [asparagine] = 0.2 mol/dm^3; $[H_2SO_4] = 3.16$ mol/dm^3; $T = 318$ K; scanning time intervals, 10 min.

Fig. 2. Reaction rate vs. time plot. $[KMnO_4] = 4 \times 10^{-4}$ mol/dm^3; [asparagine] = 0.2 mol/dm^3; $[H_2SO_4] = 3.16$ mol/dm^3; $T = 313$ K.

RESULTS

Stoichiometry and product analysis. Employing spot tests [31, 32], the final reaction products were detected as carbon dioxide, ammonium ions, and the corresponding aldehyde. At the same time, it is well known [4, 12, 33] that, in the reduction process of permanganate ions in strong acid medium while the reducing species is in excess, the Mn^{2+} ions is the final product.
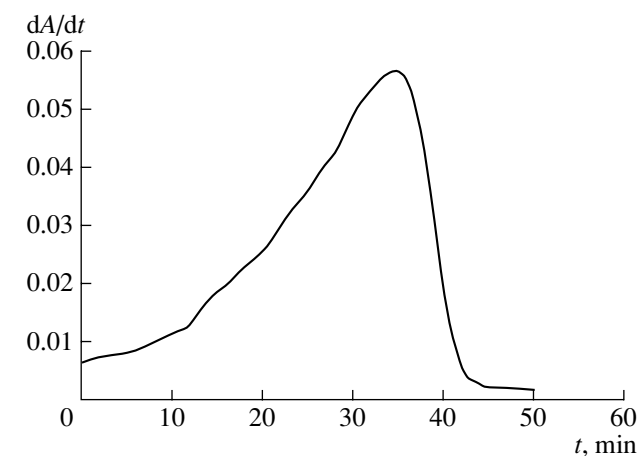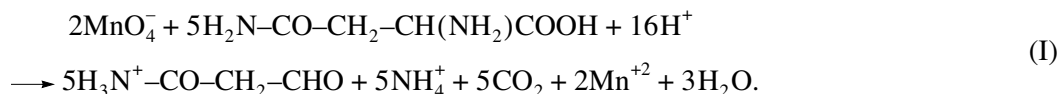
Performing our reaction in an excess of amino acid and using conventional methods to study the stoichiometry of the reaction, the following equation is proposed as the reaction stoichiometry:

$$2MnO_4^- + 5H_2N-CO-CH_2-CH(NH_2)COOH + 16H^+$$
$$\longrightarrow 5H_3N^+-CO-CH_2-CHO + 5NH_4^+ + 5CO_2 + 2Mn^{+2} + 3H_2O. \tag{I}$$

Rate equation. Figure 1 illustrates the permanganate absorption curves versus wavelength obtained at 10 min intervals as the reaction proceeds. Regarding the previous studies [15–23], Mn(IV) ions absorb in the region 400–650 nm. Figure 1 shows no features in this wavelength area, meaning that MnO$_2$ is not a reaction product. Furthermore, since no rise and fall in absorption is observed at 418 nm, it is concluded that Mn(IV) ions do not intervene as a possible oxidizing agent.

When the reaction rate is plotted against time (Fig. 2), a bell-shaped curve is obtained. Similar plots have been reported for the permanganate oxidation of compounds closely related to amino acids, e.g., aliphatic amines [34, 35].

The absorption–time plots are illustrated in Fig. 3. In all the experiments performed, curves with a sigmoid profile (Fig. 3, curve *1*) have been obtained. This characteristic suggests the existence of an autocatalytic mechanism. In order to demonstrate that Mn^{2+} is the species responsible for the autocatalytic effect, kinetics runs were carried out in the presence of the Mn^{2+} species at the beginning of the reaction. As the initial concentration of Mn^{2+} ions increased, a notable increase in the reaction rate was seen (Fig. 3, curve *2*). A further initial increase in the Mn^{2+} concentration and having it equal the permanganate ions concentration leads to a complete disappearance of the sigmoid form (Fig. 3, curve *3*). Taking the Mn^{2+} effect on the reaction rate into account, the following rate equation has been proposed:

$$d[MnO_4^-]/dt = k_1'[MnO_4^-] + k_2'[MnO_4^-][Mn^{+2}], \quad (1)$$

where k_1' and k_2' are rate pseudoconstants for noncatalytic and catalytic processes, respectively. The amino acid concentration, which is always kept in large excess, and the acid concentration, constant in each experiment, are included in these rate pseudoconstants.

The integrated form of this equation gives

$$\ln[(k_1'/k_2' + x)/(a - x)] = (k_1' + k_2'a)t - \ln(k_2'a/k_1'), (2)$$

where a represents the initial concentration of permanganate and x, the amount of permanganate ion consumed up to time t.

For the proper determination of pseudoconstants k_1' and k_2', the following procedure was employed. Since the reaction is slow and, thus, the initial Mn^{2+} concentration is sufficiently low, k_1' values have been obtained by fitting the initial portion of the rate data to a first-
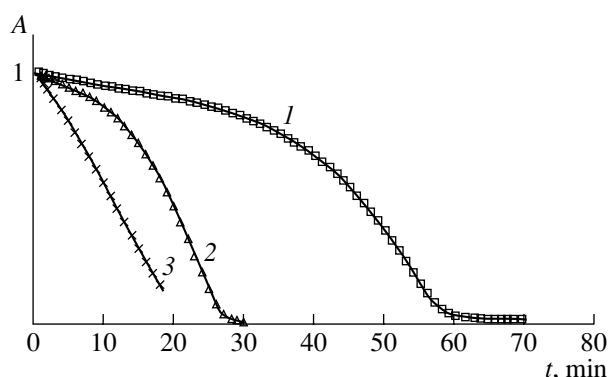
Fig. 3. Effect of the added initial concentration of ions on the absorbance time plots. $[KMnO_4] = 4 \times 10^{-4}$ mol/dm³; [asparagine] = 0.2 mol/dm³; $[H_2SO_4] = 3.16$ mol/dm³; $T = 313$ K; $[Mn^{+2}] = (1)$ 0, (2) 2×10^{-4}, and (3) 4×10^{-4} mol/dm³.

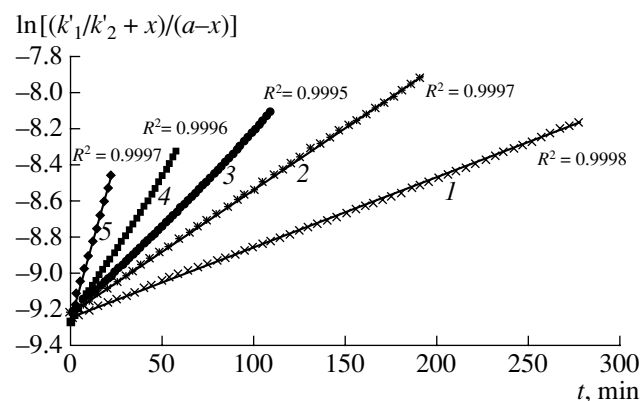**Fig. 4.** Integral rate-law plot for the oxidation of L-asparagine by potassium permanganate at various temperatures. $[KMnO_4] = 4 \times 10^{-4}$ mol/dm³; [asparagine] = 0.2 mol/dm³; $[H_2SO_4] = 3.16$ mol/dm³: (1) 298, (2) 303, (3) 308, (4) 313, and (5) 318 K.

order rate equation assuming no catalytic effect is present in the early stages of the reaction. These results are summarized in Table 1 at various temperatures. Moreover, our kinetic run in the presence of manganese sulfate(II), equal to permanganate in concentration, satisfies the following rate equation:

$$\ln[a(b + x)/b(a - x)] = k_2'(a + b)t, \qquad (3)$$

where b refers to the initial concentration of manganese sulfate(II). The calculated rate under this condition has provided a reasonable initial guess for k_2'. Having determined the k_1' value from the early stage of the reaction and obtaining a good guess for k_2', Eq. (3) has been examined for the kinetic data of the reaction [18]. Figure 4 demonstrates the results of the fitting process of rate data at various temperatures and under the same conditions.

A comparison of the k_2' values obtained by fitting the kinetic data with the initial guessed values at various temperatures has been made in Table 2. The almost prefect linearity of the curves in Fig. 4 (R_2 values 0.9995–0.9998) and the very good correspondence between the k_2' values in Table 2 not only corroborate the validity of the applied kinetic method but also confirm the autocatalytic effect of the Mn^{2+} species.

DEPENDENCE OF THE KINETIC PARAMETERS

Dependence of reaction rate on [amino acid] and $[MnO_4^-]$. The rate pseudoconstants obtained at various amino acid concentration are summarized in Table 3. Figure 5 comprises these changes. The plots of $1/k_1'$ and $1/k_2'$ against 1/[L-Asp] (not shown) gave straight lines which pass through the origin only for the former.

These observations confirm the first order and fractional order with respect to the amino acid for the non-catalytic and catalytic pathways, respectively [12].

Table 4 summarizes the data which have been obtained for k_2' in the presence of Mn^{2+} ions when the amino acid concentration is varied. From these results, it is evident that, as the amino acid concentration is raised, the reaction rate increases. This observation and the fact that the reaction is of fractional order with respect to the amino acid suggest that, in the process of permanganate consumption, some intermediate complex between Mn^{2+} and amino acid has probably been formed.

Variation of the initial concentration of permanganate showed no influence on k_1', whereas it had a negative effect on the values of k_2', as is evident from the results in Table 5.

Dependence of reaction rate on sulfuric acid concentration. The effect of $[H^+]$ ions has been investigated by means of a series of experiments carried out at various sulfuric acid concentration. As Fig. 6 shows, k_1' increases when the acid concentration is raised, whereas k_2' initially decreases and then shows a sharp increase when the acid concentration is varied. The region of 3 to 4 molar concentration of sulfuric acid

Table 1. Effect of temperature on k_1'

T, K	298	303	308	313	318
$k_1' \times 10^5$, s⁻¹	1.83	2.83	4.5	6.83	10.3

Note: $[KMnO_4] = 4 \times 10^{-4}$ mol/dm³; [asparagine] = 0.2 mol/dm³; $[H_2SO_4] = 3.16$ mol/dm³.

Table 2. Effect of Mn^{2+} on $k_2^{'}$ at different temperatures

T, K	298	303	308	313	318
$k_2^{'} \times 10^2$, dm^3/(mol s) [Mn(II)] = 0 mol/dm^3	44.63	70.97	107.92	157.47	247.52
$k_2^{'} \times 10^2$, dm^3/(mol s) [Mn(II)] = [KMnO$_4$]	44.83	70.55	107.58	157.13	247.72

Note: [KMnO$_4$] = 4×10^{-4} mol/dm^3; [asparagine] = 0.2 mol/dm^3; [H$_2$SO$_4$] = 3.16 mol/dm^3.

showed the least variation for $k_2^{'}$. Thus, this concentration region was determined as the most appropriate region for the rest of our kinetic studies.

Determination of activation parameters. As a further justification of the method that has been applied to determine the rate pseudoconstants $k_1^{'}$ and $k_2^{'}$ at various temperatures, calculated values of these parameters have been evaluated by Arrhenius and Eyring equations. Figures 7 and 8 demonstrate the obedience of both $k_1^{'}$ and $k_2^{'}$ with the Arrhenius and Eyring equations, respectively. The thermodynamic activation parameters obtained, energy, enthalpy, and entropy are reported in Table 6.

Acrylonitrile addition. The presence of free radicals as intermediates was confirmed by the addition of acrylonitrile, which led to polymerization both in the presence and absence of manganese sulfate(II).
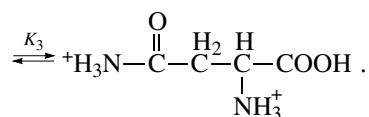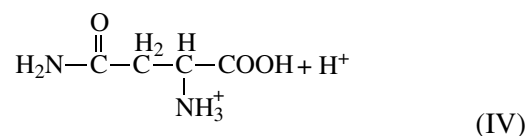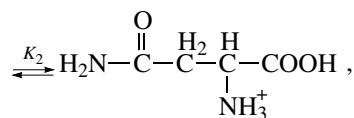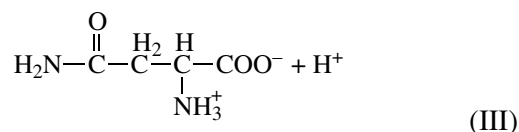
DISCUSSION

In accordance with the experimental results that have been presented and taking into account the bibliographic references, two separate mechanisms for the catalyzed and uncatalyzed pathways are proposed to interpret the reaction progress. Since the existence of

Table 3. Variation of $k_2^{'}$ and $k_1^{'}$ against the asparagine concentration

[Asparagine], mol/dm^3	$k_2^{'} \times 10^2$, dm^3/(mol s)	$k_1^{'} \times 10^5$, s^{-1}
0.1	93	3.33
0.2	157.47	6.83
0.3	216	10.33
0.4	268.83	13.67
0.5	327.67	16.5

Note: [KMnO$_4$] = 4×10^{-4} mol/dm^3; [H$_2$SO$_4$] = 3.16 mol/dm^3; T = 313 K.

intermediate free radicals was confirmed, their involvement in the reaction mechanism has also been regarded.
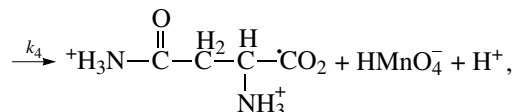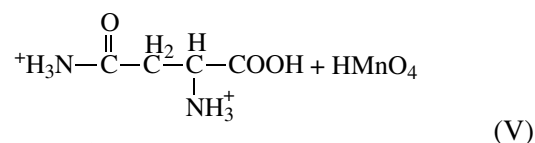
(i) Reaction mechanism for the uncatalyzed process. All the experiments were performed in a strong acid medium. With confirming evidence presented for no involvement of other manganese oxidation states, only Mn(VII) is the most probable reactive species. The reaction rate enhancement observed by increasing the acid concentration suggests the formation of a more powerful oxidant, namely, acid permanganate by the following equilibrium:

$$MnO_4^- + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} HMnO_4. \qquad (II)$$

Further protonation of amino acid gives:

(III)

(IV)

A mechanism consistent with the observed kinetic data consists of the following steps:

(V)

Fig. 5. Effect of the amino acid concentration on the catalyzed and uncatalyzed rate pseudoconstant. $[KMnO_4] = 4 \times 10^{-4}$ mol/dm^3; $[H_2SO_4] = 3.16$ mol/dm^3; $T = 313$ K.
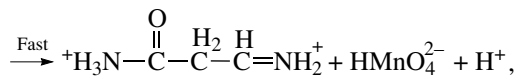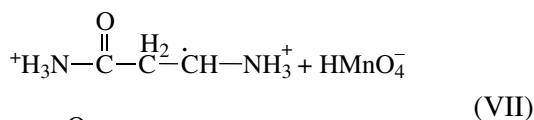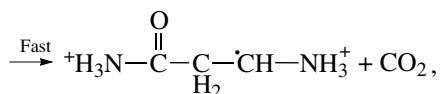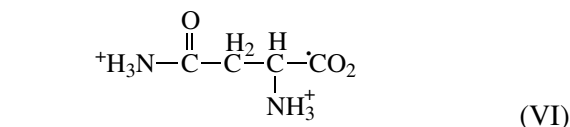

Fig. 6. Effect of the sulfuric acid concentration on the uncatalyzed and catalyzed rate pseudoconstant. $[KMnO_4] = 4 \times 10^{-4}$ mol/dm^3; [asparagine] = 0.2 mol/dm^3; $T = 313$ K.

$$\xrightarrow{Fast} {}^{+}H_3N-\overset{O}{\overset{\|}{C}}-\underset{H_2}{C}-\dot{C}H-NH_3^+ + CO_2,$$

$$(VII)$$

$$(VIII)$$

$$\xrightarrow{Fast} {}^{+}H_3N-\overset{O}{\overset{\|}{C}}-CH_2-CHO + NH_4^+,$$

$$5HMnO_4^{2-} + 11H^+ \longrightarrow 3MnO_4^- + 2Mn^{2+} + 8H_2O. \quad (IX)$$
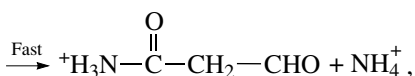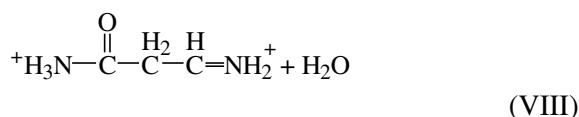
Multiplying Eqs. (II)–(VIII) by a factor of five and summing them up to Eq. (IX), results in the overall reaction with the stoichiometry satisfied. In agreement with the above scheme, the rate equation obtained for the uncatalyzed process is

$$-d[MnO_4^-]/dt = k_1'[\text{L-asparagine}][MnO_4^-], \quad (4)$$

$$k_1' = K_1 K_2 K_3 k_4 [H^+]^3/(1 + K_1[H^+]). \quad (5)$$

The rate law obtained above corresponds to that mechanism explaining the observed experimental behavior: the first-order reaction with respect to both permanganate and amino acid; no change in k_1', the uncatalyzed rate pseudoconstant, when the permanganate concentration varies.
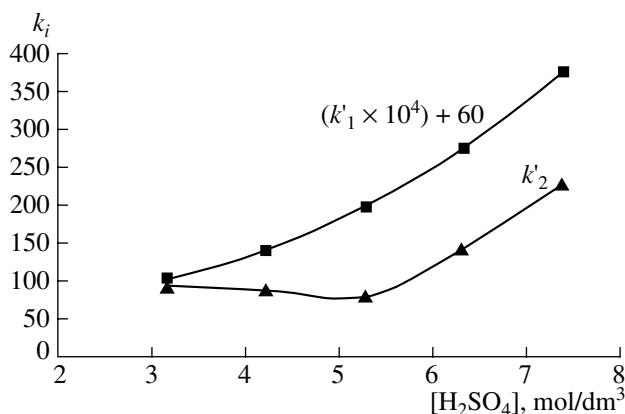
(ii) Reaction mechanism for the catalyzed process. The addition of Mn^{2+} ions not only led to an increase in the reaction rate but changed the order in [L-asparagine] from unity to fractional. The supporting evidence presented also suggests that an adduct might be formed between Mn^{2+} and the protonated L-asparagine in a fast step before it is oxidized by manganese(VII) in a slow step [15, 16]:
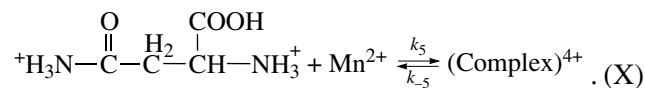
As the rate-determining step, the slow attack of the acid permanganate on the complexes has been proposed [28, 29]:

$$(\text{Complex})^{4+} + HMnO_4$$
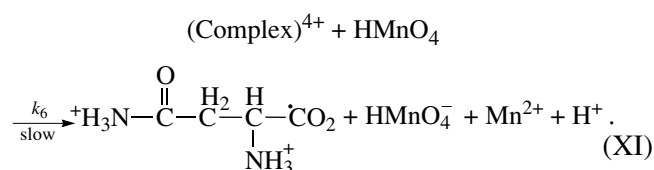
Table 4. Variation of k_2' against the asparagine acid's concentration

[Asparagine], mol/dm^3	$k_2' \times 10^2$, mol/dm^3
0.05	23.85
0.1	40.37
0.2	70.55
0.3	95.18
0.4	119.55

Note: $[KMnO_4] = 4 \times 10^{-4}$ mol/dm^3; [asparagine] = 0.2 mol/dm^3; $T = 303$ K.

The remaining steps leading to the final products resemble those presented for the uncatalyzed pathway above. Again, multiplying Eqs. (II)–(IV), (VI)–(VIII), (X), and (XI) by a factor of five and summing them up to Eq. (IX) results in the overall reaction with the correct stoichiometry. Further determination of the (complex)$^{4+}$ concentration from Eqs. (X) and (XI) would result the following rate Eq. [27]:

$$Rate = k_2'[Mn^{2+}][MnO_4^-], \quad (6)$$

$$k_2' = \frac{K_1 K_2 K_3 k_5 k_6 [\text{L-asparagine}][H^+]^3}{k_5 K_2 K_3 [H^+]^2 [\text{L-asparagine}] + k_{-5} + k_{-5} K_1 [H^+] + K_1 K_2 K_3 k_5 [H^+]^3 [\text{L-asparagine}] + K_1 k_6 [H^+][MnO_4^-]}. \quad (7)$$

This rate law, along with the one proposed for the uncatalyzed process, is in accord with all experimental results presented in this article, namely, first-order reaction in the Mn^{2+} ions, permanganate ions, and fractional order with respect to amino acid and inverse dependence of k_2' on permanganate ions concentration, which is shown in the k_2' expression [28, 29].

Due to the complexity of the proposed mechanism, evaluation of the values of the rate constants corresponding to the reaction rate determining the steps for both processes has not been possible. Thus, the activation parameters reported are associated with reaction rate pseudoconstants k_1' and k_2', and these values cannot be attributed to any particular reaction step.

Table 5. Effect of $KMnO_4$ on k_2' at different temperatures

T, K	298	303	308	313	318
$k_2' \times 10^2$, dm^3/(mol s) ([KMnO$_4$] = 4 × 10^{-4} mol/dm^3)	44.63	70.97	107.92	157.47	247.52
$k_2' \times 10^2$, dm^3/(mol s) ([KMnO$_4$] = 6 × 10^{-4} mol/dm^3)	36.87	58.72	87.28	124.65	203.75

Note: [Asparagine] = 0.2 mol/dm^3; [H$_2$SO$_4$] = 3.16 mol/dm^3.

Table 6. Activation parameters

Activation parameter	Uncatalyzed process	Catalyzed process
$\Delta S^{\#}$, J/(mol K)	−114.88 (±1.66)	−36.73 (±3.77)
$\Delta H^{\#}$, kJ/mol	65.79 (±0.51)	63.99 (±1.16)
E_a, kJ/mol	68.35 (±0.51)	66.55 (±1.16)

Note: [KMnO$_4$] = 4 × 10^{-4} mol/dm^3; [asparagine] = 0.2 mol/dm^3; [H$_2$Sé$_4$] = 3.16 mol/dm^3.
     Values in parentheses are estimated errors on each thermodynamic parameter.
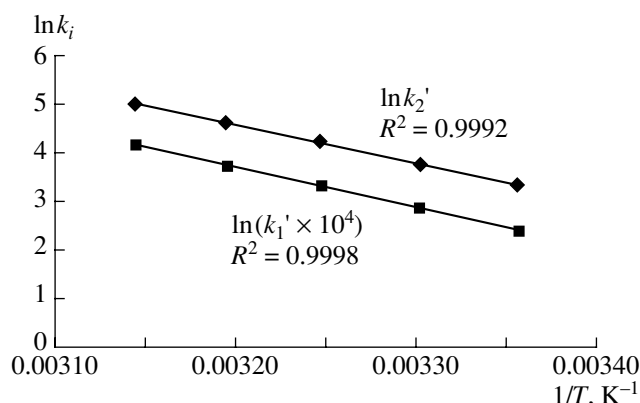
Fig. 7. Arrhenius diagram for the uncatalyzed and catalyzed process. [asparagine] = 0.2 mol/dm^3; [KMnO$_4$] = 4 × 10^{-4} mol/dm^3; [H$_2$SO$_4$] = 3.16 mol/dm^3.
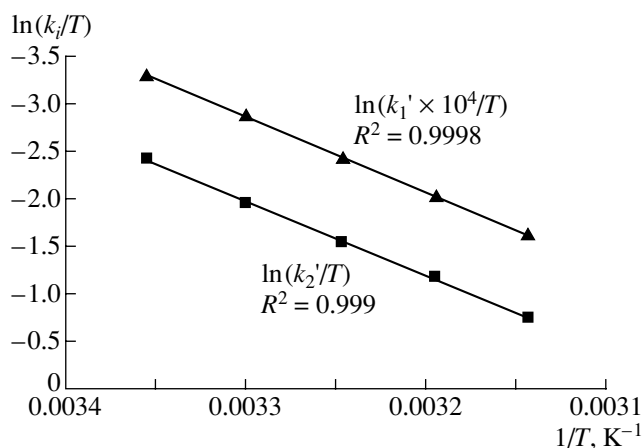
Fig. 8. Eyring diagram for the uncatalyzed and catalyzed process. [asparagine] = 0.2 mol/dm^3; [KMnO$_4$] = 4 × 10^{-4} mol/dm^3; [H$_2$SO$_4$] = 3.16 mol/dm^3.

CONCLUSIONS

The kinetics of the permanganate process of L-asparagine in a strong acid medium was investigated using the spectrophotometric technique. The addition of manganese sulfate(II) to the reaction mixture raised the reaction rate. The sigmoid profile observed for permanganate absorption variation versus time at 525 nm was completely transformed to a line under the condition [Mn(II)]$_0$ = [KMnO$_4$]. In the presence of manganese sulfate(II), by increasing the amino acid concentration, the reaction rate was increased. Thus, we report the first conclusive evidence of an autocatalytic oxidation process of an amino acid in a strong acid medium in which Mn^{2+} species are responsible for the effect. The rate pseudoconstants, obtained for both the catalytic and noncatalytic pathways while the amino acid was in excess, obeyed the Arrhenius and Eyring relations. The presence of free radicals was confirmed, and

mechanisms satisfying the experimental observations for both the catalytic and noncatalytic pathways were presented.

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