

## Kinetics and Mechanism of Oxidation of $\beta$ -Phenylalanine by Permanganate Ion in Aqueous Perchloric Acid

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The kinetics of permanganate oxidation of  $\beta$ -phenylalanine in aqueous perchlorate media at a constant ionic strength of  $3.0 \text{ mol dm}^{-3}$  has been studied spectrophotometrically. A first-order reaction in  $[\text{MnO}_4^-]$  and a fractional order with respect to  $\beta$ -phenylalanine were observed. The results obtained at various hydrogen-ion concentrations indicate that the protonated species of both the amino acid and permanganate play a role in the kinetics. Kinetic evidence for the formation of an intermediate complex between the amino acid and the oxidant is presented. The activation parameters were calculated and found to be  $\Delta S^\ddagger = -160.14 \pm 8.23 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\Delta H^\ddagger = 34.04 \pm 1.02 \text{ kJ mol}^{-1}$ , and  $\Delta G^\ddagger = 81.77 \pm 3.47 \text{ kJ mol}^{-1}$ , respectively. A mechanism consistent with the kinetic results is discussed.

Permanganate ion in acidic media has been used extensively as a potent oxidant for studying the oxidation kinetics of many organic substrates including amino acids.<sup>1-7</sup> In some cases the mechanistic approach has been based on intermediate complex formation and in others the results have been interpreted by a free-radical mechanism, in the absence of kinetic or spectrophotometric evidence. The mechanisms suggested by various authors are not uniform, indicating that a wide variety of mechanisms is possible depending on the nature of the reactive species of permanganate as well as of the amino acids.

The detailed reaction mechanism of the oxidation of  $\beta$ -phenylalanine by permanganate ion has received little attention. Rao *et al.*<sup>7</sup> have examined this reaction in sulphuric acid media and reported that the reaction kinetics were second order overall, first order with respect to the concentration of each reactant. Their results may not be a true picture of the kinetics since the presence of sulphate ions can help to stabilize  $\text{Mn}^{\text{III}}$  which may be produced during the course of reaction. Consequently, tentative conclusions regarding the nature of the reactive species were not tenable. This prompted us to investigate the kinetics of this reaction in non-complexing perchloric acid media with a view to determining the detailed reaction mechanism.

### Experimental

Stock solutions of  $\beta$ -phenylalanine and potassium permanganate were prepared by dissolving the appropriate amounts of BDH AnalaR samples in doubly distilled conductivity water. The stock solution of permanganate was standardized against  $\text{As}_2\text{O}_3$ , after which the permanganate-ion concentration was determined spectrophotometrically, immediately prior to each run, at 526 nm the absorption maximum of permanganate. The stock permanganate solution was diluted to the desired concentration before mixing using appropriate amounts of  $\text{HClO}_4$  and  $\text{NaClO}_4$  solutions.

All other reagents were of analytical grade and their solutions were prepared by dissolving the requisite amounts of the samples in doubly distilled water.

Optical density *vs.* concentration plots for acidified permanganate ion showed that Beer's law is obeyed at wavelengths of 508, 526, and 566 nm, and the molar absorption coefficients were found to be  $1.725 \pm 16$ ,  $2.230 \pm 19$ , and  $1.268 \pm 11 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ , respectively, in good agreement with previous results.<sup>8</sup>

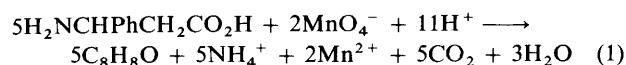
*Kinetic Measurements.*—Preliminary experiments indicated that the rate of reaction varied with the reactant concentra-

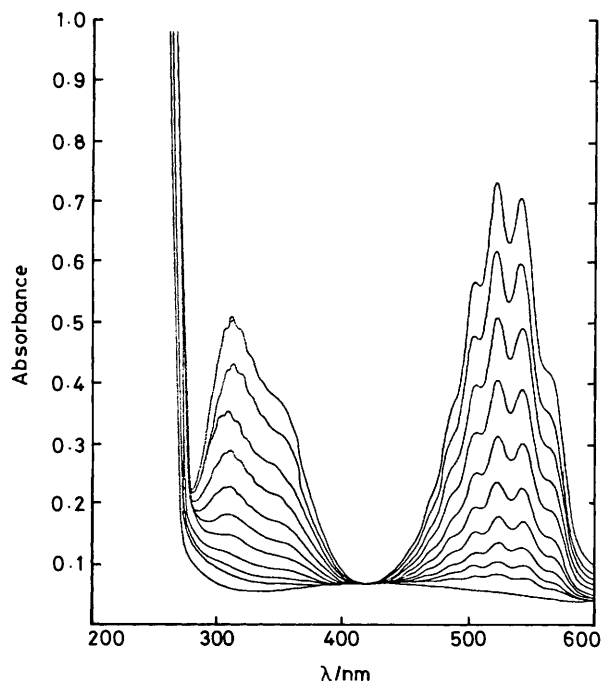
tions. The kinetic measurements were conducted under pseudo-first-order conditions where the amino acid was present in a large excess over permanganate, and at a constant ionic strength of  $3.0 \text{ mol dm}^{-3}$  (maintained with sodium perchlorate). All of the kinetic data presented in this work were obtained by using a large excess of amino acid to minimize possible further reaction of  $\text{Mn}^{2+}$  produced with the excess of  $\text{MnO}_4^-$ . Therefore the permanganate-ion concentration was not kept in a large excess so as to avoid the competitive side reactions which may complicate the reaction kinetics. The reaction solutions were thermally equilibrated in a constant-temperature water-bath maintained at the desired temperature within  $\pm 0.1^\circ \text{C}$ . When the two solutions had attained the temperature of the thermostat, the required volumes of the reactants were syringed out and poured into the reaction cell. The course of the reaction was followed by recording the decrease in absorbance of permanganate ion at its absorption maximum, 526 nm, as a function of time. It was verified that there is no interference from other reagents at this wavelength. The absorption measurements were made in a thermostatted cell compartment at the desired temperature on a Shimadzu UV double-beam spectrophotometer using cells of pathlength 1 cm.

The observed first-order rate constants,  $k_{\text{obs}}$ , with respect to permanganate ion were calculated from the gradients of linear plots of  $\ln(\text{absorbance})$  *vs.* time. The reaction was generally followed beyond two half-lives. The linearity of these plots beyond this point indicates that none of the products formed during the reaction affected the rate. The spectral changes during the redox reaction are shown in Figure 1. The gradients of such plots were calculated by the least-squares method.

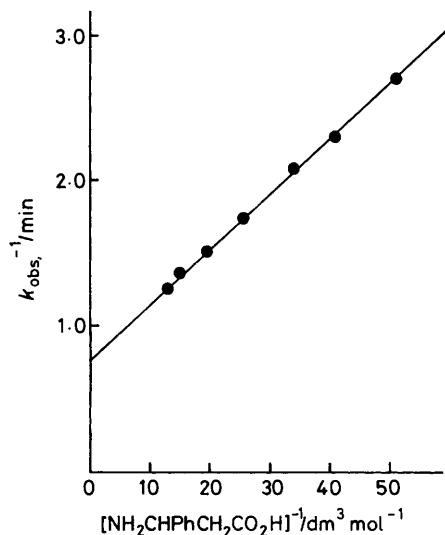
### Results

*Stoichiometry and Product Analysis.*—Reaction mixtures containing various ratios of amino acid to  $\text{MnO}_4^-$  were mixed in the presence of  $3.0 \text{ mol dm}^{-3}$   $\text{HClO}_4$  adjusted to constant ionic strength, then equilibrated for 24 h at room temperature. Estimation of the unreacted  $[\text{MnO}_4^-]$  showed that 1 mol of  $\text{MnO}_4^-$  consumed  $2.5 \pm 0.1$  mol of the amino acid. Product analysis indicated the formation of ammonium ion and an aldehyde. This result confirms that the stoichiometry of the overall reaction is as in equation (1). Aldehyde and ammonium





**Figure 1.** Spectral changes in the oxidation of  $\beta$ -phenylalanine by permanganate ion at  $[\text{MnO}_4^-] = 3.4 \times 10^{-4}$ ,  $[\text{NH}_2\text{CHPhCH}_2\text{CO}_2\text{H}] = 7.9 \times 10^{-3}$ ,  $[\text{H}^+] = 2.5$ ,  $I = 3.0 \text{ mol dm}^{-3}$ , scanning time intervals = 3 min, and  $25^\circ\text{C}$



**Figure 2.** Representative Michaelis-Menten plot for the oxidation of  $\beta$ -phenylalanine by permanganate ion at  $[\text{MnO}_4^-] = 3.4 \times 10^{-4}$ ,  $[\text{H}^+] = 3.0 \text{ mol dm}^{-3}$ , and  $30^\circ\text{C}$

ions were detected in the reaction mixture by simple qualitative tests.<sup>9,10</sup> The formation of aldehyde as a reaction product was found to be in accord with the oxidation of some other amino acids by permanganate ion.<sup>5,6</sup>

**$[\text{MnO}_4^-]$  and [amino acid] Dependences.**—The reaction order with respect to permanganate ion was determined by studying the oxidation reaction at  $25^\circ\text{C}$  under the conditions  $[\text{amino acid}]_0 = 0.02$ ,  $[\text{MnO}_4^-]_0 = 3.4 \times 10^{-4}$ , and  $[\text{H}^+] = 2.0 \text{ mol dm}^{-3}$ . Plots of  $\ln(\text{absorbance})$  versus time were linear to 90% completion of reaction giving  $k_{\text{obs.}} = 14 \times 10^{-2} \text{ min}^{-1}$ .

**Table 1.** Effect of added  $\text{Mn}^{2+}$  on the observed rate constant at  $[\text{MnO}_4^-] = 3.4 \times 10^{-4}$ ,  $[\text{NH}_2\text{CHPhCH}_2\text{CO}_2\text{H}] = 0.02$ ,  $[\text{H}^+] = 3.0 \text{ mol dm}^{-3}$ , and  $25^\circ\text{C}$

$10^4[\text{Mn}^{2+}]/\text{mol dm}^{-3}$	0	1.0	2.0	4.0	6.0	8.0	10
$k_{\text{obs.}}/\text{min}^{-1}$	0.30	0.28	0.24	0.20	0.17	0.14	0.10

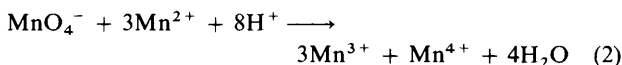
**Table 2.** Effect of ionic strength on the observed rate constant at  $[\text{MnO}_4^-] = 3.4 \times 10^{-4}$ ,  $[\text{NH}_2\text{CHPhCH}_2\text{CO}_2\text{H}] = 0.02$ ,  $[\text{H}^+] = 2.0 \text{ mol dm}^{-3}$ , and  $25^\circ\text{C}$

$I/\text{mol dm}^{-3}$	2.5	3.0	3.5	4.0	4.5
$k_{\text{obs.}}/\text{min}^{-1}$	0.11	0.13	0.16	0.18	0.20

The linearity shows that the reaction is first order in  $[\text{MnO}_4^-]$ . This first-order dependence was indicated not only by the linearity of the pseudo-first-order plots, but also by the independence of the observed first-order rate constants,  $k_{\text{obs.}}$ , on different initial  $[\text{MnO}_4^-]_0$  values varied from  $2 \times 10^{-4}$  to  $8 \times 10^{-4} \text{ mol dm}^{-3}$  in a number of steps at constant concentrations of all other reagents.

The dependence of the  $k_{\text{obs.}}$  values on the amino acid concentration was found to follow Michaelis-Menten kinetics.<sup>11</sup> A typical reciprocal Michaelis-Menten plot is shown in Figure 2. The good linearity obtained in addition to the positive intercept of the  $k_{\text{obs.}}^{-1}$  axis indicates formation of an intermediate complex in the reaction between  $\text{MnO}_4^-$  and  $\beta$ -phenylalanine.

**Dependence of Reaction Rate on Added Salts.**—Since  $\text{Mn}^{2+}$  is one of the oxidation products, its effect on the rate of reaction was investigated. It is reported<sup>12,13</sup> that acidified permanganate ion is reduced by  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  according to equation (2). It was found that variation of  $[\text{Mn}^{2+}]_0$  had an



appreciable effect on the rate of reaction. As the initial concentration of  $\text{Mn}^{2+}$  increased the rate progressively decreased. The data are summarized in Table 1. This result indicates that neither  $\text{Mn}^{3+}$  nor  $\text{Mn}^{4+}$  is involved in the oxidation process.

The effects of pyrophosphate and fluoride ions on the rate of reaction were also investigated. Addition of either sodium pyrophosphate or sodium fluoride does not affect the reaction rate significantly. This also means that  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  are not reactive species under the experimental conditions, since if they were the reaction would exhibit an induction period or decrease in rate following the addition of such complexing agents. The absence of such behaviour indicates that  $\text{MnO}_4^-$  is probably the only reactive species responsible for the oxidation process.

In view of the pronounced effect of  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  on the rate of permanganate oxidation of organic substrates, it was considered of interest to examine their possible catalytic effects. The rate of reaction was found to be unaffected by adding the perchlorate salts of  $\text{Ag}^+$  and  $\text{Cu}^{2+}$  (up to  $2 \times 10^{-2} \text{ mol dm}^{-3}$ ) to the reaction mixture in  $3.0 \text{ mol dm}^{-3} \text{ HClO}_4$  at  $25^\circ\text{C}$ . This lack of a catalytic effect indicates that  $\text{Mn}^{\text{VII}}$  is directly reduced to  $\text{Mn}^{\text{V}}$  without formation of  $\text{Mn}^{\text{VI}}$  as an intermediate.

**Dependence of Reaction Rate on Ionic Strength.**—In order to investigate the effect of ionic strength on the rate of reaction, kinetic runs were performed at  $[\text{H}^+] = 2.0 \text{ mol dm}^{-3}$  with increasing addition of  $\text{NaClO}_4$  up to  $4.5 \text{ mol dm}^{-3}$ . The values of  $k_{\text{obs.}}$  were found to increase with increasing ionic strength (Table 2). A plot of  $\ln k_{\text{obs.}}$  against  $I^{\frac{1}{2}}$  according to the Debye-Hückel equation<sup>14</sup> was linear with a positive intercept.

**Table 3.** Effect of hydrogen-ion concentration on the observed rate constant at  $[\text{MnO}_4^-] = 3.4 \times 10^{-4}$ ,  $[\text{NH}_2\text{CHPhCH}_2\text{CO}_2\text{H}] = 0.02$ ,  $I = 3.0 \text{ mol dm}^{-3}$ , and  $25^\circ\text{C}$

$[\text{H}^+]/\text{mol dm}^{-3}$	3.0	2.75	2.5	2.25	2.0
$10^2 k_{\text{obs.}}/\text{min}^{-1}$	30.3	25.6	21.1	17.2	13.5

However, the present measurements, of necessity, lie far outside the Debye-Hückel region, covering a range over which the activity coefficients of many electrolytes are known to be fairly dependent on ionic strength.<sup>15</sup> The ionic strength dependence is qualitatively as expected when considering the charges involved.<sup>16</sup>

*Dependence of Reaction Rate on the Hydrogen-ion Concentration.*—To clarify the influence of  $[\text{H}^+]$  on the rate of reaction and to elucidate the reaction mechanism, kinetic measurements were performed in  $\text{HClO}_4$ - $\text{NaClO}_4$  solutions of different  $[\text{H}^+]$  and constant ionic strength and temperature. An increase in the acid concentration was found to accelerate the reaction rate. When the observed first-order rate constants were plotted against  $[\text{H}^+]^2$  straight lines passing through the origin were obtained. The values of  $k_{\text{obs.}}$  calculated are summarized in Table 3.

The possibility of the formation of free radicals was examined by adding acrylonitrile to the partially oxidized reaction mixture. No polymerization occurred, *i.e.* the reaction does not proceed by a free-radical mechanism.

## Discussion

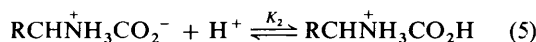
Kinetic evidence of the formation of an intermediate complex was provided not only by the Michaelis-Menten plot (Figure 2), but also by a slight increase in the optical density over that of the initial amino acid observed in the u.v. region on mixing with permanganate ion at *ca.*  $5^\circ\text{C}$ . Reactions between a metal ion and a ligand such as an amino acid seem to proceed *via* initial complex formation<sup>17</sup> rather than simple second-order kinetics as reported elsewhere.<sup>7</sup> In the oxidation of other amino acids<sup>5,6</sup> by permanganate ion, it was suggested that the faster rate of oxidation at higher hydrogen-ion concentrations is most probably due to the protonation of the oxidant. This suggestion was supported by spectral studies<sup>18</sup> which were in accord with the equilibrium (3) where  $K_1 = 2.99 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1}$  at



$25^\circ\text{C}$ .<sup>19</sup> It is well known that amino acids in aqueous solution exist as zwitterions [equation (4)]. In concentrated acidic

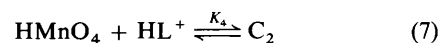
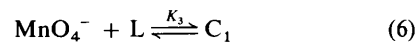


media, zwitterions exist predominantly as the protonated species<sup>20</sup> according to the equilibrium (5). Our observations

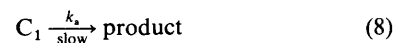


lead us to suggest that  $\text{HMnO}_4$  and  $\text{HL}^+$  (where  $\text{HL}^+$  represents the protonated form of  $\beta$ -phenylalanine) are the reactive species in the rate-determining step. This suggestion is consistent with the observed kinetics. The positive slope of the plot of  $\ln k_{\text{obs.}}$  versus  $I^{1/2}$  indicates that the rate-determining step may be a reaction between an ion and a neutral molecule.<sup>21</sup>

The two most likely reaction mechanisms which may be suggested involve the two competitive reactions (6) and (7). The



intermediates  $\text{C}_1$  and  $\text{C}_2$  are formed and subsequently undergo further dissociation to give the products [equations (8) and (9)].



Considering that reactions (8) and (9) are the rate-determining steps, the change in the rate constant with change in the hydrogen-ion concentration may be expressed by equation (10)

$$\frac{d[\text{MnO}_4^-]}{dt} = \frac{(k_a K_3 + k_b K_1 K_2 K_4 [\text{H}^+]^2) [\text{L}] [\text{MnO}_4^-]_{\text{T}}}{1 + K_1 [\text{H}^+] + [\text{L}] (K_3 + K_1 K_2 K_4 [\text{H}^+]^2)} \quad (10)$$

where  $[\text{MnO}_4^-]_{\text{T}}$  is the total concentration of permanganate ion. In the presence of a large excess of amino acid over that of permanganate, the rate law is as in equation (11). Comparison

$$-d[\text{MnO}_4^-]/dt = k_{\text{obs.}} [\text{MnO}_4^-] \quad (11)$$

of equations (10) and (11) thus yields the relation (12).

The experimental results described here are not in agreement with the rate equation (12), since plots of  $k_{\text{obs.}}$  against  $[\text{H}^+]^2$

$$k_{\text{obs.}} = \frac{k_a K_3 + k_b K_1 K_2 K_4 [\text{H}^+]^2 [\text{L}]}{1 + K_1 [\text{H}^+] + [\text{L}] (K_3 + K_1 K_2 K_4 [\text{H}^+]^2)} \quad (12)$$

gave good straight lines passing through the origin. This means that the first term corresponding to the unprotonated species of equation (6) is relatively small and hence reaction (6) can be neglected. Reaction (7) may therefore be considered as the sole mechanism, and the rate equation can now be written as in (13).

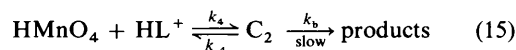
$$\frac{1}{k_{\text{obs.}}} = \left( \frac{[\text{H}^+]^2}{k_b K_1 K_2 K_4} + \frac{[\text{H}^+]}{k_b K_2 K_4} \right) \frac{1}{[\text{L}]} + K' \quad (13)$$

According to equation (13), at constant  $[\text{H}^+]$  a plot of  $k_{\text{obs.}}^{-1}$  versus  $[\text{L}]^{-1}$  should be a straight line, as is experimentally observed (Figure 2). Again, a plot of  $[\text{H}^+]/k_{\text{obs.}}$  against  $1/[\text{H}^+]$  at constant  $[\text{L}]$  gave a good straight line with a negligible intercept on the  $[\text{H}^+]/k_{\text{obs.}}$  axis. Hence, equation (13) may be simplified to (14), which is considered as the appropriate rate

$$\frac{[\text{H}^+]}{k_2} = \frac{[\text{H}^+]}{k_b'} + \frac{1}{k_b''} \quad (14)$$

equation for the oxidation of  $\beta$ -phenylalanine by permanganate ion, where  $k_b' = k_b K_1 K_2 K_4$ ,  $k_b'' = k_b K_2 K_4$ , and  $k_2 = k_{\text{obs.}}/[\text{L}]$ .

An alternative reaction mechanism might also be suggested on the basis of the decomposition of the intermediate complex  $\text{C}_2$  in the rate-limiting step, equation (15). In view of this



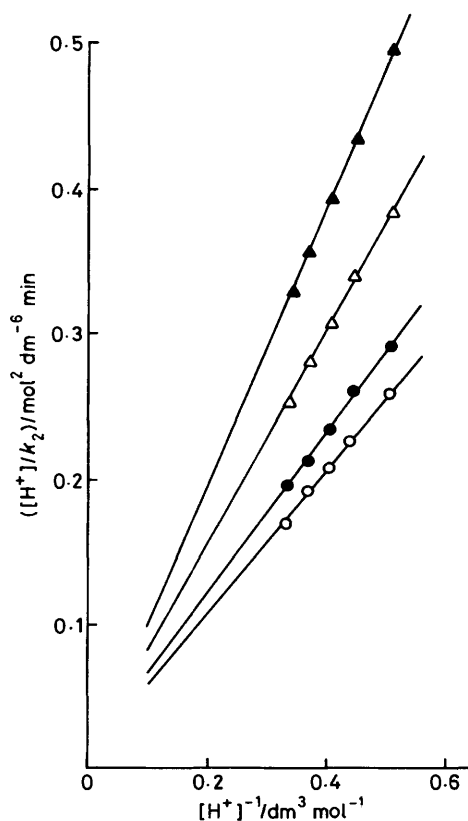
comment and applying the steady-state treatment to the intermediate complex  $\text{C}_2$  under the condition  $k_b \gg k_{-4}[\text{C}_2]$ , a rate equation similar to that of (14) can be obtained.

*Dependence of Reaction Rate on Temperature.*—To determine the activation parameters, the reaction was carried out at four temperatures between 15 and  $30^\circ\text{C}$  and at constant ionic

**Table 4.** Activation parameters for some permanganate reactions

Reagent	$\Delta S^\ddagger/\text{J K}^{-1}\text{mol}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta G^\ddagger/\text{kJ mol}^{-1}$	Ref.
$\beta$ -Phenylalanine <sup>a</sup>	-160	34	82	This work
Glycine	-116	48	83	4
DL-Valine	-105	51	82	4
DL-Alanine	-53	70	86	4
L-Arginine	-127	50	88	6
Substituted benzylamines	-92	49	76	24
Formic acid <sup>a</sup>	-79	69	92	25
H <sub>2</sub>	-54	61	78	18
CO <sup>a</sup>	-71	54	76	18
CN <sup>-a</sup>	-113	36	70	b
Br <sup>-a</sup>	-124	26	63	18
I <sup>-a</sup>	-60	16	78	29

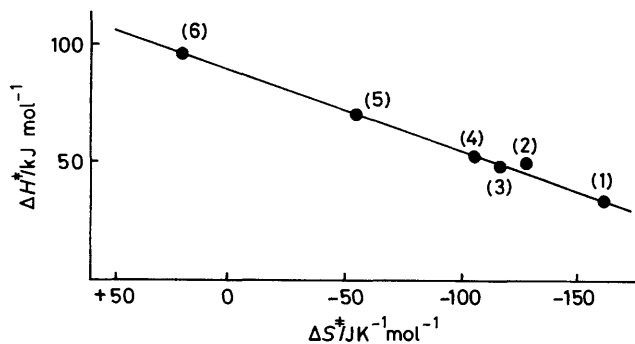
<sup>a</sup> Complex-formation mechanism. <sup>b</sup> R. Stewart and R. Vand der Linden, *Can. J. Chem.*, 1960, **38**, 2237.



**Figure 3.** Plot of  $([\text{H}^+]/k_2)$  versus  $1/[\text{H}^+]$  at  $I = 3.0 \text{ mol dm}^{-3}$  and 28 (O), 25 (●), 20 (Δ), and 15 °C (▲)

strength and hydrogen-ion concentration. A plot of the Eyring equation<sup>22</sup> gave a good straight line from whose slope and intercept the enthalpy and entropy of activation were determined. The activation parameters were calculated by the least-squares method and are compared in Table 4 with results for other systems.

Equation (14) indicates that a plot of  $([\text{H}^+]/k_2)$  versus  $[\text{H}^+]^{-1}$  should be linear. The available data satisfied this requirement as shown in Figure 3. The protonation constants  $K_1$  can be evaluated from the slope and intercept of such plots. The value of  $K_1$  at 25 °C was calculated to be  $0.00292 \text{ dm}^3 \text{ mol}^{-1}$  in good agreement with a value reported elsewhere.<sup>19</sup>



**Figure 4.** Isokinetic relationship,  $\Delta H^\ddagger$  vs.  $\Delta S^\ddagger$ , for the oxidation of some amino acids by permanganate ion. Acids: (1)  $\beta$ -phenylalanine; (2) L-arginine;<sup>6</sup> (3) glycine;<sup>4</sup> DL-valine;<sup>4</sup> (5) DL-alanine;<sup>4</sup> (6) DL-leucine<sup>4</sup>

Unfortunately, the value of  $k_b$  could not be evaluated because of non-availability of the protonation constant  $K_2$  and the formation constant  $K_4$ . Although some attempts were made to evaluate these constants from the experimental data, the results were not satisfactory. Therefore, the apparent rate constants  $k_b'$  and  $k_b''$  are considered to be products of the rate constants, the protonation and the formation constants.

The activation parameters corresponding to  $k_b'$  were calculated (Table 4). The entropy of activation for the decomposition of the intermediate permanganate-amino acid complex in the rate-determining step was found to be negative, in accord with the proposition made by Stewart and co-workers<sup>18,23</sup> for ionic transition states. It is of interest that the entropy of activation,  $\Delta S^\ddagger$ , is negative for the group of  $\text{MnO}_4^-$  reactions for which the investigators either present direct evidence or postulate complex formation between  $\text{Mn}^{\text{VII}}$  and the reductant species, while the values of  $\Delta S^\ddagger$  of the reactions of  $\text{MnO}_4^-$  with a few outer-sphere reacting compounds tend to be more positive.

The absence of a catalytic effect on the rate of this reaction may be considered as evidence for two-electron reduction of permanganate ion, leading to the formation of  $\text{Mn}^{\text{V}}$  as an intermediate. This pathway is also the more favoured from the kinetic standpoint, while the alternative of an initial one-electron transfer is much less probable on the energetic grounds. Therefore it appears that the oxidation of  $\beta$ -phenylalanine by permanganate ion proceeds *via* complex formation and a two-electron transfer. Arguments have also been presented in several cases for oxidation of organic substrates by this oxidant which proceed by similar reaction mechanisms.<sup>18,24-27</sup>

The kinetic parameters for some organic and inorganic reactions which possess negative entropies of activation are also summarized in Table 4. Leffler and Grunwald<sup>28</sup> have pointed out that many reactions show an isokinetic relationship  $\Delta H^\ddagger = C + B\Delta S^\ddagger$ . As shown in Figure 4, a plot of  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$  for some reactions of amino acids with permanganate is fairly linear, with  $C = 108 \text{ kJ mol}^{-1}$  and  $B = 330 \text{ K}$ . This linearity indicates that the kinetics of the oxidation of these amino acids may follow similar reaction mechanisms. Also, the  $B$  value obtained is significant and reflects the reactivity of these amino acids.

Moreover, the oxidation of some inorganic substrates such as  $\text{Br}^-$ ,<sup>18</sup>  $\text{CN}^-$ ,<sup>19</sup>  $\text{I}^-$ ,<sup>29</sup>  $\text{Cl}^-$ ,<sup>30</sup> and  $[\text{Co}(\text{NH}_3)_5(\text{O}_2\text{CH})]^{2+}$ <sup>31,32</sup> by  $\text{MnO}_4^-$  has been interpreted in terms of complex formation between manganese(vii) species and the reductant, with subsequent formation of a manganese(v) species.

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