

# Kinetics of the Oxidative Degradation of *rac*-Serine by Aqueous Alkaline Permanganate

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**Summary.** The kinetics of the oxidation of *rac*-serine by permanganate in aqueous alkaline medium was studied spectrophotometrically. The reaction showed first order kinetics in permanganate ion concentration and an order less than unity in *rac*-serine and alkali concentration. Increasing ionic strength and decreasing dielectric constant of the medium increase the rate. The oxidation reaction proceeds *via* an alkali-permanganate species which forms a complex with *rac*-serine. The latter decomposes slowly, followed by a fast reaction between a free radical of *rac*-serine and another molecule of permanganate to give the products. There is a good agreement between the observed and the calculated rate constants under different experimental conditions. Investigations at different temperatures allowed the determination of the activation parameters with respect to the slow step of the proposed mechanism.

**Keywords.** *rac*-Serine; Alkaline permanganate; Oxidation; Kinetics.

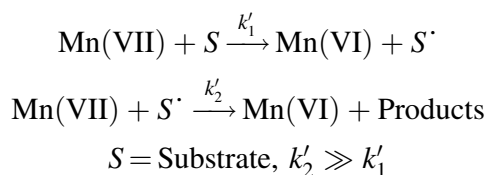
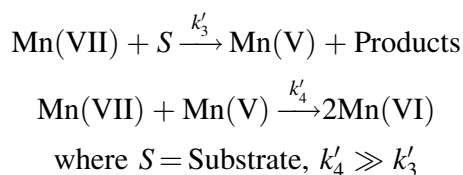
## Introduction

Oxidation by permanganate has been extensively applied in organic syntheses [1–7], especially since the advent of phase-transfer catalysis [3, 4, 6] which permits the use of solvents such as methylene chloride and benzene. Kinetic studies constitute an important source of mechanistic information on the reaction, as demonstrated by results referring to unsaturated acids in both aqueous [1,3,7] and non-aqueous media [8].

The manganese chemistry involved in these multistep redox reactions is an important source of information. The manganese intermediates are relatively easy to identify provided they have sufficiently long life times, and the oxidation states of the intermediates permit useful conclusions concerning the reaction mechanism, including the nature of intermediates.

In strongly alkaline medium, the stable reduction product of the permanganate ion is the manganate ion [9]. No mechanistic information is available to distinguish between a direct one-electron reduction to Mn (VI) (Scheme 1) or a prior formation of hypomanganate in a two-electron step followed by a fast reaction (Scheme 2).

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**Scheme 1****Scheme 2**

*rac*-Serine is an important non-essential amino acid with an OH-substituted side chain. The hydroxyl group plays an integral role in the function of several proteins like enzymes, hormones, glycoproteins, lipoproteins, *etc.* Serine is a crucial part of the chymotrypsin enzyme, maintaining the proper ionic state of the active site for the interaction with substrates at particular *pH* values.

Although some work on the oxidation of organic [10] and inorganic [11] substrates by permanganate in aqueous alkaline medium has been carried out, there is no report in the literature on the oxidation of *rac*-serine in such media. This reaction has therefore been carried out in order to elucidate the redox chemistry of permanganate in alkaline media and to derive a plausible mechanism.

**Results and Discussion***Reaction order*

The reaction orders have been determined from the slopes of  $\log k_{\text{obs}}$  vs.  $\log c$  plots by varying the concentrations of oxidant, reductant, and alkali in turn while keeping the others constant. The potassium permanganate concentration was varied in the range of  $5.0 \times 10^{-5}$  to  $5.0 \times 10^{-4}$  mol · dm<sup>-3</sup>, and the linearity of the plots of  $\log [\text{MnO}_4^-]$  vs. time ( $r > 0.9989$ ,  $S \leq 0.032$ ) indicated a reaction order of unity in  $[\text{MnO}_4^-]$ . This was also confirmed by variation of  $[\text{MnO}_4^-]$  which did not result in any change in the *pseudo*-first-order rate constants  $k_{\text{obs}}$  (Table 1). The substrate concentration was varied in the range of  $5.0 \times 10^{-4}$  to  $5.0 \times 10^{-3}$  mol · dm<sup>-3</sup> at 25°C while keeping all other reactant concentrations and conditions constant. The reaction order in [*rac*-serine] was found to be less than unity (0.76, Table 1).

*Effect of initially added reaction products*

Products of the oxidation reaction such as manganate, ammonia, and aldehyde added at the beginning of the sequence together with the educts did not show any significant effect on the rate of the reaction.

**Table 1.** Effect of [*rac*-serine],  $[\text{MnO}_4^-]$  and  $[\text{OH}^-]$  on the oxidation of *rac*-serine by permanganate in aqueous alkaline medium at 25°C ( $I=0.6 \text{ mol} \cdot \text{dm}^{-3}$ )

$\frac{[\text{DL} - \text{serine}] \times 10^3}{\text{mol} \cdot \text{dm}^{-3}}$	$\frac{[\text{MnO}_4^-] \times 10^4}{\text{mol} \cdot \text{dm}^{-3}}$	$\frac{[\text{OH}^-]}{\text{mol} \cdot \text{dm}^{-3}}$	$k_{\text{obs}} \times 10^3/\text{s}^{-1}$	
			Exptl.	Calc.
0.5	2.0	0.3	1.15	1.24
1.0	2.0	0.3	2.10	2.20
2.0	2.0	0.3	3.50	3.63
3.0	2.0	0.3	4.70	4.61
5.0	2.0	0.3	5.90	5.87
2.0	0.5	0.3	3.50	3.48
2.0	1.0	0.3	3.48	3.50
2.0	2.0	0.3	3.50	3.63
2.0	3.0	0.3	3.40	3.38
2.0	5.0	0.3	3.42	3.40
2.0	2.0	0.05	1.32	1.33
2.0	2.0	0.10	2.13	2.14
2.0	2.0	0.30	3.50	3.63
2.0	2.0	0.40	3.90	3.97
2.0	2.0	0.50	4.18	4.21

### Effect of alkali

The effect of alkali on the reaction has been studied at constant concentrations of *rac*-serine and potassium permanganate and a constant ionic strength of  $0.6 \text{ mol} \cdot \text{dm}^{-3}$  at 25°C. The rate constant increased with increasing alkali concentration (Table 1; order = 0.5).

### Effect of solvent polarity and ionic strength

The effect of relative permittivity ( $\epsilon_T$ ) on the rate constant has been studied by varying the *t*-butanol-water content in the reaction mixture with all other conditions being maintained constant. Attempts to measure the relative permittivities were not successful. However, they were computed from the values of pure liquids as already performed earlier [12]. No reaction of the solvent with the oxidant occurred under the experimental conditions employed. The rate constant  $k_{\text{obs}}$  increased with decreasing dielectric constant of the medium. The plot of  $\log k_{\text{obs}}$  vs.  $1/\epsilon_T$  was linear (Fig. 1  $r > 0.9994$ ,  $S \leq 0.081$ ).

The effect of ionic strength was studied by variation the  $\text{NaClO}_4$  concentration in the reaction medium. The ionic strength was varied from 0.3 to  $1.5 \text{ mol} \cdot \text{dm}^{-3}$  at constant concentrations of permanganate, *rac*-serine, alkali. It was found that the rate constant increased with increasing concentration of  $\text{NaClO}_4$ ; the plot of  $\log k_{\text{obs}}$  vs.  $I^{1/2}$  was linear ( $r > 0.9389$ ,  $S \leq 0.014$ ) with a positive slope (Fig. 1).

### Test for free radicals

To test for the presence of free radicals, the reaction mixture was mixed with acrylonitrile and kept in an inert atmosphere for 24 h. Dilution with methanol

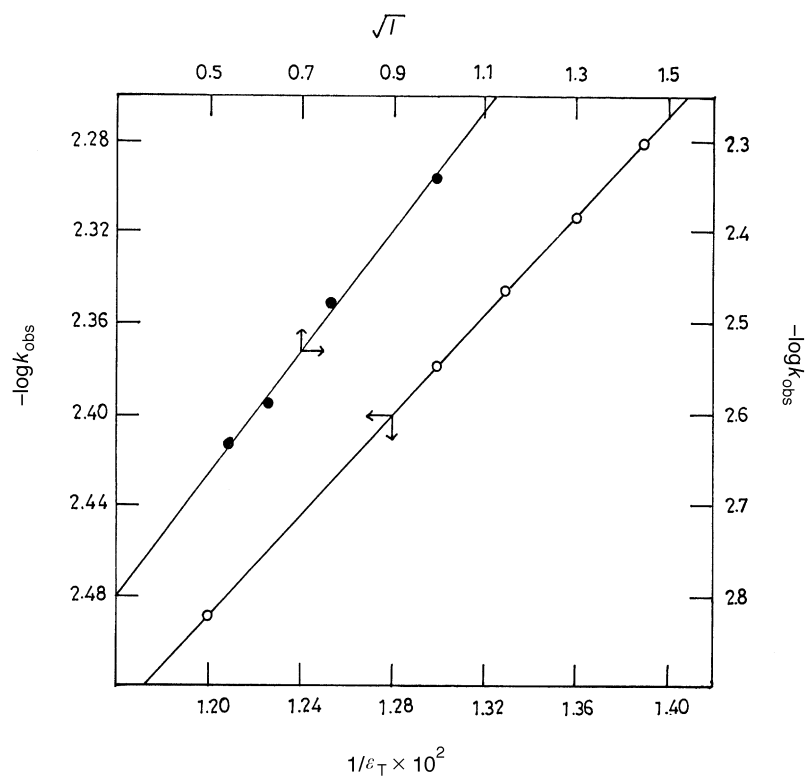
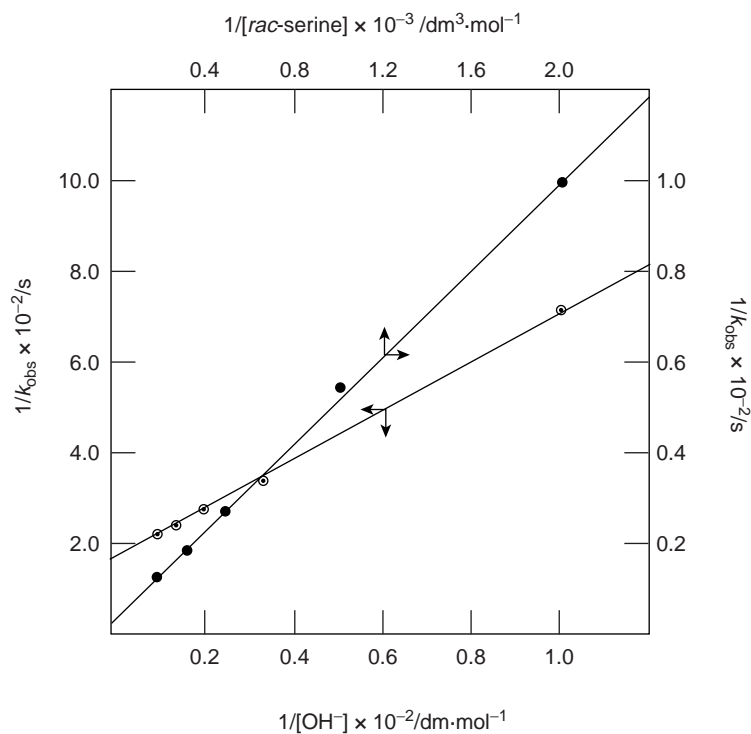


Fig. 1. Plots of  $\log k_{\text{obs}}$  vs.  $I^{1/2}$  and  $\log k_{\text{obs}}$  vs.  $1/\epsilon_T$

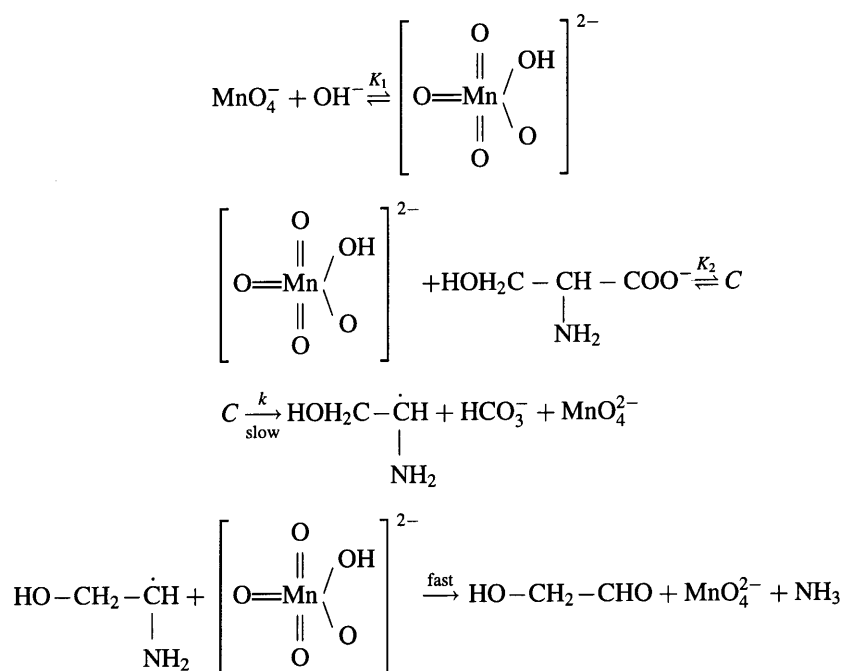
induced the formation of a white precipitate, indicating the participation of free radicals in the reaction.

The permanganate ion is a powerful oxidant in aqueous alkaline medium. As manganese exhibits a multitude of oxidation states, the stoichiometry and the  $pH$  of the reaction medium play an important role in the determination of products. Under the present experimental conditions ( $pH > 12$ ) the reduction product of Mn(VII), *i.e.* Mn(VI), is stable, and further reduction is not to be expected [11]. Diode array rapid scan spectrophotometric studies have shown that at  $pH > 12$  Mn(VII) is reduced to Mn(VI), and no further reduction has been observed [11]. However, upon prolonged standing Mn(VI) is slowly reduced to Mn(IV) under our experimental conditions.

The reaction between *rac*-serine and permanganate in alkaline medium has a stoichiometry of 1:2 with an order of less than unity for both alkali and *rac*-serine and a first-order dependence on  $[\text{MnO}_4^-]$ . No effect of the product was observed. The results suggest that the alkali combines first with permanganate to give an alkali-permanganate species  $[\text{MnO}_4 \cdot \text{OH}]^{-2}$  in a prior equilibrium step [14] which is also supported by the observed fractional order in  $[\text{OH}^-]$  and the *Michaelis-Menten* plot (Fig. 2) which is linear with a positive intercept. The permanganate species then reacts with the substrate in its deprotonated form [13] to give a complex *C* which decomposes in a slow step to a free radical derived from decarboxylated *rac*-serine. This radical in turn reacts with another molecule of permanganate in a fast step to yield the products (Scheme 3).

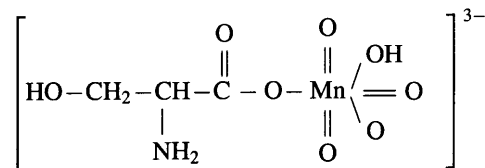


**Fig. 2.** Plots of  $1/k_{\text{obs}}$  vs.  $1/[\text{OH}^-]$  and  $1/k_{\text{obs}}$  vs.  $1/[\text{rac-serine}]$  (conditions as in Table 1)



**Scheme 3**

A suggestion for a probably structure of complex *C* is given below:



Spectroscopic evidence for the complex formation between oxidant and substrate was obtained from UV/Vis spectra of the substrate and mixtures of substrate and oxidant. A bathochromic shift of about 7 nm from 226 to 233 nm is observed, and hyperchromicity is observed at  $\lambda_{\text{max}}$  of about 233 nm. Analogous effects upon complex formation between a substrate and an oxidant have been observed in other investigations [15]. The formation of the complex is proved kinetically by the non-zero intercept of the plot of  $1/k_{\text{obs}}$  vs.  $1/[\textit{rac-serine}]$ . The observed modest enthalpy of activation and a relatively low value of the entropy of activation as well as a higher rate constant of the slow step indicate that the oxidation presumably occurs *via* an inner-sphere mechanism. This conclusion is supported by earlier observations [16]. Since Scheme 3 is in accordance with the generally well accepted principle of non-complementary oxidations taking place in a sequence of one-electron steps, the reaction between the substrate and oxidant would afford a radical intermediate. A free radical scavenging experiment corroborated this assumption. The same type of radical intermediate has also been observed earlier in the context of alkaline permanganate oxidation of various amino acids [17].

The thermodynamic parameters of the first step of Scheme 3 and the activation parameters for the rate determining step of Scheme 3 could be evaluated as follows: the hydroxyl ion concentration was varied at several temperatures, and values of  $K_1$  were determined at each temperature. The values of  $K_1$  obtained are 2.80, 3.72, 5.52, and 7.36  $\text{dm}^3 \cdot \text{mol}^{-1}$  at 25, 30, 35, and 40°C, respectively. A *van't Hoff* plot was drawn for the variation of  $K_1$  with temperature ( $\log K_1$  vs.  $1/T$ ;  $r > 0.9993$ ,  $S \leq 0.018$ ), and values for  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  of  $51.0 \pm 2.5 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $-53 \pm 2.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ , and  $67 \pm 3.3 \text{ kJ} \cdot \text{mol}^{-1}$  were derived. An *Arrhenius* plot of  $\log k$  vs.  $1/T$  ( $r > 0.9997$ ,  $S \leq 0.019$ ) yielded the activation parameters for the rate limiting step of Scheme 3 which are given in Table 2. A comparison of the latter values with those obtained for the slow step of the reaction shows that these values mainly refer to the rate limiting step, supporting the fact that the reaction before the rate determining step is fairly rapid and involves only little activation energy.

Scheme 3 leads to the rate law given in Eq. (1).

$$v = -\frac{d[\text{MnO}_4^-]}{dt} = \frac{k \cdot K_1 \cdot K_2 \cdot [\textit{rac-serine}] \cdot [\text{MnO}_4^-] \cdot [\text{OH}^-]}{1 + K_1[\text{OH}^-] + K_1 \cdot K_2 \cdot [\textit{rac-serine}] \cdot [\text{OH}^-]} \times \frac{1}{(1 + K_1 \cdot K_2 \cdot [\text{MnO}_4^-] \cdot [\text{OH}^-])(1 + K_1 \cdot [\text{MnO}_4^-] + K_1 \cdot K_2 \cdot [\textit{rac-serine}] \cdot [\text{MnO}_4^-])} \quad (1)$$

The terms  $(1 + K_1 \cdot K_2 \cdot [\text{MnO}_4^-] \cdot [\text{OH}^-])$  and  $(1 + K_1 \cdot [\text{MnO}_4^-] + K_1 \cdot K_2 \cdot [\textit{rac-serine}] \cdot [\text{MnO}_4^-])$  in the denominator of Eq. (1) approximate to unity in view

of the low concentration of  $\text{MnO}_4^-$  used ( $K_1 = 2.8$  and  $K_2 = 625$ ). Therefore, Eq. (1) becomes

$$v = -\frac{d[\text{MnO}_4^-]}{dt} = \frac{k \cdot K_1 \cdot K_2 \cdot [\text{rac-serine}] \cdot [\text{MnO}_4^-] \cdot [\text{OH}^-]}{1 + K_1 \cdot [\text{OH}^-] + K_1 \cdot K_2 \cdot [\text{rac-serine}] \cdot [\text{OH}^-]} \quad (2)$$

or

$$\frac{v}{[\text{MnO}_4^-]} = k_{\text{obs}} = \frac{k \cdot K_1 \cdot K_2 \cdot [\text{rac-serine}] \cdot [\text{OH}^-]}{1 + K_1 \cdot [\text{OH}^-] + K_1 \cdot K_2 \cdot [\text{rac-serine}] \cdot [\text{OH}^-]} \quad (3)$$

Equation (3) can be rearranged to the following form which is used for the verification of the rate law:

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k \cdot K_1 \cdot K_2 \cdot [\text{rac-serine}] \cdot [\text{OH}^-]} + \frac{1}{k \cdot K_2 \cdot [\text{rac-serine}]} + \frac{1}{k} \quad (4)$$

According to Eq. (4), the plots of  $1/k_{\text{obs}}$  vs.  $1/[\text{rac-serine}]$  ( $r > 0.9996$ ,  $S \leq 0.078$ ) and  $1/k_{\text{obs}}$  vs.  $1/[\text{OH}^-]$  should be linear which is verified in Fig. 2. ( $r > 0.9999$ ,  $S \leq 0.021$ ). The slopes and intercepts of the plots lead to values of  $k$ ,  $K_1$ , and  $K_2$  at  $25^\circ\text{C}$  of  $0.01 \pm 0.0006 \text{ s}^{-1}$ ,  $2.80 \pm 0.14 \text{ dm}^3 \cdot \text{mol}^{-1}$ , and  $625 \pm 31 \text{ dm}^3 \cdot \text{mol}^{-1}$ , respectively. Using these values, the rate constants under different experimental conditions were calculated and compared with experimental data (Table 1). Experimental and calculated values agree reasonably well supporting the assumptions of Scheme 3. The value of  $K_1$  is in good agreement with that derived in earlier work [14].

### Effect of temperature

The rate constants of the slow step of Scheme 3 were obtained from the intercept of the plot of  $1/k_{\text{obs}}$  vs.  $1/[\text{rac-serine}]$  ( $r > 0.9996$ ,  $S \leq 0.056$ ) at different temperatures and used to calculate the activation parameters (Table 2). The values of  $k(\text{s}^{-1})$  were 0.010, 0.014, 0.020, and 0.028 at 25, 30, 35, and  $40^\circ\text{C}$ , respectively. The corresponding activation parameters are shown in Table 2.

The effect of ionic strength on the rate qualitatively explains the reaction between the charged ions of similar kind as shown in Scheme 3. The effect of solvent on the reaction kinetics has been described in detail in the literature [18-23]. Increasing the content of *t*-butanol in the reaction medium leads to an increase

**Table 2.** Thermodynamic activation parameters for the oxidation of *rac*-serine by alkaline permanganate with respect to the slow step of Scheme 3

Parameter	Value
$E_a/\text{kJ} \cdot \text{mol}^{-1}$	$51 \pm 2$
$\log A$	$7.8 \pm 0.4$
$\Delta H^\ddagger/\text{kJ} \cdot \text{mol}^{-1}$	$49 \pm 3$
$\Delta S^\ddagger/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$-28 \pm 2$
$\Delta G^\ddagger/\text{kJ} \cdot \text{mol}^{-1}$	$58 \pm 3$

**Table 3.** Activation parameters for some amino acids

	$k_{\text{obs}} \times 10^3/\text{s}^{-1}$ (298 K)	$k_{\text{obs}} \times 10^3/\text{s}^{-1}$ (309 K)	$\Delta S^\ddagger/$ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta H^\ddagger/$ $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta G^\ddagger/$ $\text{kJ} \cdot \text{mol}^{-1}$	Reference
<i>L</i> -Arginine	0.76	1.16	-190	18	76	33
<i>L</i> -Aspartic acid	4.00	7.10	-99	40	55	34
<i>L</i> -Glutamic acid	2.22	6.13	-86	45	19	35
<i>rac</i> -serine	10.00	14.00	-28	49	57	present work

in the rate of reaction which seems to be contrary to the expected interaction between neutral and anionic species in media of lower relative permittivity. However, an increase in the rate of reaction with decreasing dielectric constant may be due to stabilization of the trivalent complex *C* at low relative permittivity which is less solvated than  $\text{MnO}_4^-$  at higher dielectric constant because of its larger size. The moderate values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  are both favourable for electron transfer processes. Negative values of  $\Delta S^\ddagger$  for radical reactions have been ascribed to the nature of electron pairing and unpairing processes and to the loss of degrees of freedom by formation of a rigid transition state [24].

The activation parameters for the oxidation of some amino acids by  $\text{MnO}_4^-$  are summarized in Table 3. The entropy of activation for the  $\text{MnO}_4^-$  – *rac*-serine reaction falls within the observed range. Variation in the rate within a reaction series may be caused by changes in the enthalpy and/or entropy of activation. Changes in the rate are caused by changes in both  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ , but these quantities vary extensively in a parallel fashion. A plot of  $\Delta H^\ddagger$  vs.  $\Delta S^\ddagger$  is linear according to Eq. (5).

$$\Delta H^\ddagger = \beta \cdot \Delta S^\ddagger + \text{constant} \quad (5)$$

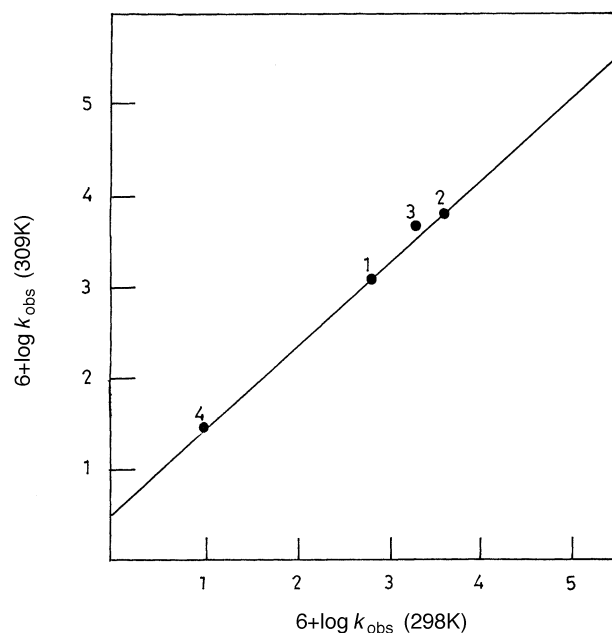
$\beta$  is called the isokinetic temperature; it has been asserted that apparently linear correlations of  $\Delta H^\ddagger$  with  $\Delta S^\ddagger$  are sometimes misleading and that the evaluation of  $\beta$  by means of Eq. (5) lacks statistical validity [25]. *Exner* [26] advocates an alternative method for the treatment of experimental data. If the rates of several reactions in a series have been measured at two temperatures and  $\log k_2$  (at  $T_2$ ) is linearly related to  $\log k_1$  (at  $T_1$ ), *i.e.*  $\log k_2 = a + b \cdot \log k_1$ , he proposes that  $\beta$  be evaluated from Eq. (6).

$$\beta = \frac{T_1 T_2 \cdot (b - 1)}{b \cdot T_2 - T_1} \quad (6)$$

We have calculated the isokinetic temperature as 424 K by plotting  $\log k_{\text{obs}}$  at 298 K vs.  $\log k_{\text{obs}}$  at 309 K (Fig. 3,  $r > 0.9989$ ,  $S \leq 0.021$ ). The value of  $\beta$  (424 K) is much higher than the experimental temperature (298 K). The linearity and the slope of the plot obtained may confirm that the kinetics of these reactions follow similar reaction mechanisms, as previously suggested.

It is also interesting that the oxidant species  $[\text{MnO}_4^-]$  required a  $pH > 12$  below which the system becomes disturbed and the reaction proceeds to Mn(VI) which slowly develops yellow turbidity.





**Fig. 3.** Isokinetic relationship of *Exner's* plot for oxidation of some amino acids by  $\text{MnO}_4^-$ : 1: *L*-arginine, 2: *L*-aspartic acid, 3: *L*-glutamic acid, 4: *rac*-serine

Hence, it becomes apparent that in carrying out this reaction the role of *pH* in the reaction medium is crucial. It is also noteworthy that under the conditions studied the reaction occurs in two successive one-electron reduction steps (Scheme 3) rather than in a single step two-electron reduction (Scheme 2).

## Experimental

### *Materials*

Stock solutions of *rac*-serine (Sisco) and  $\text{KMnO}_4$  (BDH) were prepared by dissolving the appropriate amounts of samples in doubly distilled  $\text{H}_2\text{O}$ . The stock solution of permanganate was standardized against oxalic acid [27]. A  $\text{K}_2\text{MnO}_4$  solution was prepared as described by *Carrington and Symons* [28] as follows: A solution of  $\text{KMnO}_4$  was heated to boiling in 8.0 *M* potassium hydroxide solution until a green colour appeared. The solid formed on cooling was recrystallized from the same solvent. Using the required amount of recrystallized sample, a stock solution of  $\text{K}_2\text{MnO}_4$  was prepared in aqueous potassium hydroxide. The solution was standardized by measuring the absorbance using a Hitachi Model 150-20 spectrophotometer with a 1 cm cell at 608 nm ( $\epsilon = 1530 \pm 20 \text{ dm}^3 \cdot \text{mol}^{-1} \text{ cm}^{-1}$ ).

All other reagents were of analytical grade, and their solutions were prepared by dissolving the required amount of sample in doubly distilled conductivity water.  $\text{NaOH}$  and  $\text{NaClO}_4$  were used to provide the required basicity and ionic strength, respectively.

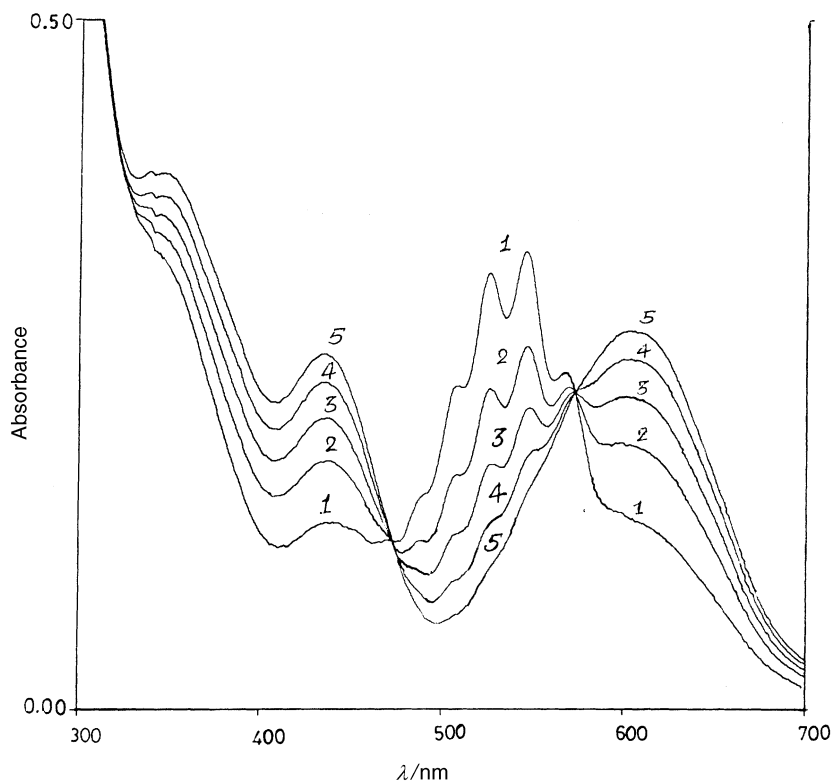
### *Kinetic measurements*

All kinetic measurements were performed under *pseudo*-first-order conditions with *rac*-serine in at least 10-fold excess over permanganate ion at a constant ionic strength of  $0.60 \text{ mol} \cdot \text{dm}^{-3}$ . The reaction was initiated by mixing previously thermostatted solutions of  $\text{MnO}_4^-$  and *rac*-serine which

also contained the necessary quantities of NaOH and NaClO<sub>4</sub> to maintain the required basicity and ionic strength. The temperature was maintained at 25±0.1°C. The course of the reaction was followed by monitoring the decrease in the absorbance of MnO<sub>4</sub><sup>-</sup> in a 1 cm quartz cell at its absorption maximum (526 nm) as a function of time. Earlier it has been verified that there is negligible interference from the other reagents at this wavelength. The application of *Beer's* law to permanganate at 526 nm has also been verified, giving  $\epsilon = 2083 \pm 50 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  (literature:  $\epsilon = 2200 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ [9]). The first-order rate constant  $k_{\text{obs}}$  were evaluated by plots of  $\log [\text{MnO}_4^-]$  vs. time. The first-order plots were linear up to 80% completion of the reaction in almost all cases and the  $k_{\text{obs}}$  values were reproducible within ±5%.

In the course of the measurements, the colour of the solution changed from violet to blue and further to green. The spectrum of the green solution was identical with that of MnO<sub>4</sub><sup>2-</sup>. Probably, the blue colour originated from the violet of MnO<sub>4</sub><sup>-</sup> and the green of MnO<sub>4</sub><sup>2-</sup>, excluding the accumulation of hypomanganate. The formation of Mn(VI) was also confirmed by a decreasing absorbance of Mn(VII) at 526 nm and an increasing absorbance of Mn(VI) at 608 nm during the course of the reaction (Fig. 4). The effect of dissolved O<sub>2</sub> on the rate of reaction was checked by preparing the reaction mixture and following the reaction in an atmosphere of N<sub>2</sub>. No significant difference between the results was observed. In view of the ubiquitous contamination of basic solutions by carbonate, the effect of carbonate on the reaction was also studied. Added carbonate had no effect on the reaction rate. However, fresh solutions were used during the experiments.

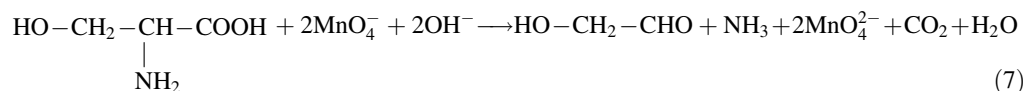
Regression analysis of experimental data to obtain the regression coefficient  $r$  and the standard deviation  $S$  of points from the regression line was performed using a PC.



**Fig. 4.** Spectroscopic changes occurring in the oxidation of *rac*-serine by permanganate with  $[\text{MnO}_4^-] = 2.2 \times 10^{-4}$ ,  $[\text{rac-serine}] = 2.0 \times 10^{-3}$ ,  $[\text{OH}^-] = 0.3$ , and  $I = 0.6 \text{ mol} \cdot \text{dm}^{-3}$  at 25°C (scanning time interval: 1 min)

*Stoichiometry*

The reaction mixture containing excess permanganate over *rac*-serine was mixed in the presence of  $0.3 \text{ mol} \cdot \text{dm}^{-3}$  NaOH adjusted to a constant ionic strength of  $0.6 \text{ mol} \cdot \text{mol} \cdot \text{dm}^{-3}$  and allowed to react for about 4 h at  $25 \pm 0.1^\circ\text{C}$ . The remaining permanganate was then analyzed spectrophotometrically. The results indicated that two moles of  $\text{MnO}_4^-$  were consumed by one mole of *rac*-serine according to Eq. (7).



The reaction products were eluted with ether, and organic products were submitted to spot tests [29] and chromatographic analysis [30] which revealed the presence of hydroxyacetaldehyde. The presence of aldehyde was also confirmed by IR spectroscopy which showed bands at  $3463\text{--}3431$  and  $1727\text{--}1730 \text{ cm}^{-1}$  for OH and C=O stretching, respectively, whereas the band at  $2925\text{--}2930 \text{ cm}^{-1}$  is due to aldehydic stretching [31]. Ammonia was identified with *Nessler's* reagent [32] and manganate by its UV/Vis spectrum. It was further observed that the aldehyde does not undergo further oxidation under the present conditions.

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