Kinetic Study of Homogeneous Acid-catalysed Oxidation of Certain Amino-acids by Potassium Permanganate in Moderately Concentrated Acidic Media

By **Radhey S. Verma, Madhusudana J. Reddy,** and **Vyayendra R. Shastry,*** School of Studies in Chemistry, Vikram University, Ujjain (M.P.), India

The rate of oxidation of glycine, DL-alanine, DL-valine, and DL-leucine by potassium permanganate in aqueous sulphuric and perchloric acid solution is proportional to the concentration of the amino-acid. For each amino-acid, the total order of the reaction is two at a given concentration of sulphuric and perchloric acid. The rate of oxidation of the amino-acids is greater in sulphuric than in perchloric acid for the same concentration. Various hypotheses for the mechanism of acid catalysis have been tested and it has been found that the rate is related to the activity of water in accord with Bunnett's hypothesis. There is no primary salt effect, but at higher concentrations of added neutral salts, the logarithm of the rate constant is linearly related to ionic strength. Specific ionic effects have also been found. The energy and entropy of activation and frequency factor have been calculated and a mechanism in agreement with the observations is suggested.

ALTHOUGH a great deal of work has been done [1-4] on the kinetics and mechanism of oxidation of various organic compounds by potassium permanganate, the oxidation of amino-acids by this powerful oxidant has received little attention.[5-10] The present paper deals with this problem.

EXPERIMENTAL

Crystalline glycine (Fabriques De Laire), DL-alanine (B.D.H.), DL-valine (Merck), and DL-leucine (Reanal) were used. Potassium permanganate, sulphuric acid, and chemicals other than those below were B.D.H. AnalaR products. Perchloric acid 'GR' was supplied by Merck. Caesium sulphate was supplied by Hopkin and Williams. Doubly distilled water was used to prepare all solutions.

Solutions of amino-acids were prepared directly by weighing. Potassium permanganate solution was prepared by the method of Vogel.[11] Stock solutions of sulphuric and perchloric acid were standardized against previously standardized sodium hydroxide solution.

Kinetic Measurements.—(i) Reactions were carried out in glass-stoppered bottles from which light was excluded at constant temperature (±0.1°). Solutions of the substrate, sulphuric or perchloric acid, and of salt (when studying salt or specific ionic effects) were mixed and the mixture brought to constant temperature. An appropriate volume of potassium permanganate solution, previously thermostatted, was then mixed rapidly with the solution. Zero time was taken when half the permanganate solution had been added. The kinetics was measured using a Lange colorimeter, model J, at 525 nm. Portions (2 ml) of the reaction mixture were withdrawn at known intervals and the reaction was quenched by adding it to a known excess of ice-cold distilled water ($<2°$) in the optical cell. The absorbance due to unchanged permanganate was read directly from the colorimeter. The absorbance at 525 nm of products in reactions which were 99% complete was negligible. The initial concentration of permanganate was low compared with those of the other reactants. Pseudo-first-order rate constants (k_1) are the average from 2—3 runs, for the first 70—75, 60—65, 50—55, and 45—50% of the reaction for glycine, DL-alanine, DL-valine, and DL-leucine, respectively. The results were reproducible to

---

[1] J. W. Ladbury and C. F. Cullis, *Chem. Rev.*, 1958, **58**, 403.

[2] W. A. Waters, *Quart. Rev.*, 1958, **12**, 277.

[3] A. Carrington and M. C. R. Symons, *Chem. Rev.*, 1963, **63**, 443.

[4] R. Stewart in ' Oxidation in Organic Chemistry,' ed. K. B. Wiberg, Academic Press, New York, 1965, Part A (*a*) pp. 1—68; (*b*) p. 48; (*c*) p. 31.

[5] O. G. Pokrovskaya, *Izvest. sibirsk. Otdel Akad. Nauk S.S.S.R.*, 1959, **8**, 50.

[6] Z. Kovats, *Magyar Kém. Folyiórat*, 1960, **66**, 181.

[7] K. Kumar and L. K. Saxena, *J. Indian Chem. Soc.*, 1970, **47**, 435.

[8] Govind Chandra, Ph.D. Thesis, Agra University, 1971.

[9] Govind Chandra and S. N. Shrivastava, *Indian J. Chem.*, 1973, **11**, 773.

[10] J. K. Sthapak and S. Ghosh, *J. Indian Chem. Soc.*, 1970, **47**, 347.

[11] A. I. Vogel, 'A Text Book of Quantitative Inorganic Analysis,' Longman Green, London, 1964, p. 282.

within 4%. The standard mean deviation is 0.0155 and coefficient of standard deviation is 0.0025.

RESULTS AND DISCUSSION

Order of Reaction.—It is observed that at constant concentrations of sulphuric or perchloric acid and substrate, the order of reaction with respect to permanganate is one. The values of pseudo-first-order rate constants k_1 for various concentrations of potassium permanganate are given in Table 1.

TABLE 1

Variation of rate constant with concentration of $KMnO_4$ at 30°

$10^4[KMnO_4]$/M	5.0	7.5	10.0	12.5
(i) Glycine (0.4M)				
10^3k_1/min^{-1} (3M-H_2SO_4)	10.42	10.31	10.28	10.35
10^3k_1/min^{-1} (3M-$HClO_4$)	8.69	8.77	8.80	8.75
(ii) DL-Alanine (0.4M)				
10^3k_1/min^{-1} (4M-H_2SO_4)	9.45	9.27	9.23	9.32
10^3k_1/min^{-1} (4M-$HClO_4$)	5.86	5.92	5.98	5.80
(iii) DL-Valine (0.2M)				
10^3k_1/min^{-1} (4M-H_2SO_4)	10.94	10.82	10.90	10.88
(iv) DL-Leucine (0.01M)				
10^3k_1/min^{-1} (4M-H_2SO_4)	7.96	7.92	7.92	7.84
10^3k_1/min^{-1} (4M-$HClO_4$)	3.10	3.06	3.06	3.13

Plots of rate constants against amino-acid concentrations give straight lines passing through the origin for both sulphuric and perchloric acid, thus showing that the order of reaction with respect to substrate is one in both the acidic media. There is no kinetic evidence for intermediate complex formation between substrate and permanganate;[12] if any complex is formed, its formation constant would be extremely small.[13] The results are summarized in Table 2.

TABLE 2

Variation of the rate constant with concentration of substrate at 30°

[Acid] 4.0M; [$KMnO_4$] 10^{-3}M

[Glycine]/M	0.1	0.2	0.3	0.4	0.5
10^3k_1/min^{-1} (H_2SO_4)	7.02	13.39	19.77	28.66	35.20
10^3k_1/min^{-1} ($HClO_4$)	4.58	9.06	12.77	18.81	22.63
[DL-Alanine]/M	0.1	0.2	0.3	0.4	0.5
10^3k_1/min^{-1} (H_2SO_4)	2.42	4.85	7.19	9.23	11.58
10^3k_1/min^{-1} ($HClO_4$)	1.57	2.98	4.46	5.98	7.69
[DL-Valine]/M	0.05	0.10	0.15	0.20	0.25
10^3k_1/min^{-1} (H_2SO_4)	3.47	5.59	8.12	10.90	14.19
10^3[DL-Leucine]/M	1.0	1.5	2.0	2.5	3.0
10^3k_1/min^{-1} (H_2SO_4)	7.92	10.79	13.11	16.81	21.01
10^3k_1/min^{-1} ($HClO_4$)	3.06	4.02	5.35	6.50	7.92

Effect of Acid Concentration and Acid Catalysis.—In general the amino-acids exist predominantly as the protonated species in concentrated acidic media according to equilibrium (1).[14]

$$NH_2CHRCO_2H \underset{}{\overset{\text{Aqueous}}{\rightleftharpoons}} \overset{+}{N}H_3CHRCO_2^- \overset{\text{H+ (Acidic)}}{\rightleftharpoons} \overset{+}{N}H_3CHRCO_2H \qquad (1)$$

Increases in acid concentration also increase the rate of oxidation of amino-acids (Table 3). In the case of oxidation of alcohols by permanganate, it was suggested that the faster rate of oxidation in more concentrated sulphuric acid is most probably due to protonation of the oxidant[4b] [equilibrium (2)]. Similar observations

$$MnO_4^- + H^+ \rightleftharpoons HMnO_4 \qquad (2)$$

in the present case lead us to suggest that $HMnO_4$ is the active oxidizing species for both sulphuric and perchloric acid. Also the fact that the rate of oxidation is strictly proportional to the concentration of the substrate indicates that $HMnO_4$ oxidizes the substrate directly.[15]

TABLE 3

Effect of increasing acid concentration on the reaction rate at 30°

[Glycine] 0.4M; [$KMnO_4$] 10^{-3}M

[Acid]/M	3.0	3.5	4.0	4.5	5.0
10^3k_1/min^{-1} (H_2SO_4)	10.28	17.23	28.66	48.50	83.71
10^3k_1/min^{-1} ($HClO_4$)	8.80	11.66	18.81	35.09	56.98

[DL-Alanine] 0.2M; [$KMnO_4$] 10^{-3}M

[Acid]/M	4.0	4.5	5.0	5.5	6.0	7.0
10^3k_1/min^{-1} (H_2SO_4)	3.97		6.21		11.70	19.58
10^3k_1/min^{-1} ($HClO_4$)	2.98	3.97	5.27	7.06	9.86	

[DL-Valine] 0.2M; [$KMnO_4$] 10^{-3}M

[Acid]/M	3.0	3.5	4.0	4.5	5.0
10^3k_1/min^{-1} (H_2SO_4)	4.88	7.72	10.90	19.51	30.39

[DL-Leucine] 0.01M; [$KMnO_4$] 10^{-3}M

[Acid]/M	3.5	4.0	4.5	5.0	5.5	6.0
10^3k_1/min^{-1} (H_2SO_4)	4.78	7.92	16.04	32.54	60.67	116.30
10^3k_1/min^{-1} ($HClO_4$)		3.06	6.04	10.87	23.99	42.38

In an attempt to correlate the rate of oxidation with acid concentration further, various hypotheses for the mechanism of acid catalysis were tested. For the oxidation of these four amino-acids by permanganate both the Zucker–Hammett plots *i.e.* log k_1 against $-H_0$ and log k_1 against log [Acid] are linear. This shows that the reaction is acid catalysed. A summary of the various Zucker–Hammett[16] plots is reported in Table 4. However, none of the plots produces the ideal slope of unity.

In view of these departures from ideal values applicability of Bunnett's hypothesis was tested (Figures 1 and 2). A summary of the slopes (ω and ω^*) for the two Bunnett plots *i.e.* log $k_1 + H_0$ against log a_{H_2O} and log k_1 − log [Acid] against log a_{H_2O} is given in Table 4. According to Bunnett's empirical observations the values in both sulphuric and perchloric acid indicate that the water molecule should act as a proton abstracting agent in the rate-determining step.[17]

The values of Hammett's acidity function, H_0, and logarithm of activity of water corresponding to given

---

[12] R. N. Mehrotra, *J. Chem. Soc.* (*B*), 1968, 1123.

[13] P. S. Sankhla and R. N. Mehrotra, *Indian J. Chem.*, 1972, **10**, 1081, 2077.

[14] R. T. Morrison and R. N. Boyd, 'Organic Chemistry,' Prentice Hall, New Delhi, 1973, p. 1102.

[15] G. V. Bakore, R. Dayal, and P. Nath, *Z. phys. Chem.* (*Leipzig*), 1964, **227**, 19.

[16] L. Zucker and L. P. Hammett, *J. Amer. Chem. Soc.*, 1939, **61**, 2791.

[17] J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4968.

TABLE 4

Correlation of rate with acid concentration

Correlation	Slope						
	Glycine		DL-Alanine		DL-Valine	DL-Leucine	
	H_2SO_4	$HClO_4$	H_2SO_4	$HClO_4$	H_2SO_4	H_2SO_4	$HClO_4$
Zucker–Hammett plots							
H_0 against log k_1	0.9	0.9	0.6	0.5	0.9	1.2	1.1
log [Acid] against log k_1	3.8	4.6	*a*	2.8	*a*	6.7	6.8
Bunnett plots							
log k_1 + H_0 against log a_{H_2O}	*a*	*a*	−2.6	−3.10	*a*	*a*	*a*
log k_1 − log [Acid] against log a_{H_2O}	5.3	4.9	1.9	1.70	4.3	5.9	4.5

[a] No straight line obtained.

acid concentrations have been taken from Paul and Long[18] and Bunnett[19] respectively.

Effect of Temperature.—The reactions were studied at 25, 30, 35, 40, and 45° for the oxidation of all four amino-acids. Energies of activation ΔE, entropies of activation ΔS, and frequency factors, PZ, for the reactions are summarized in Table 5.

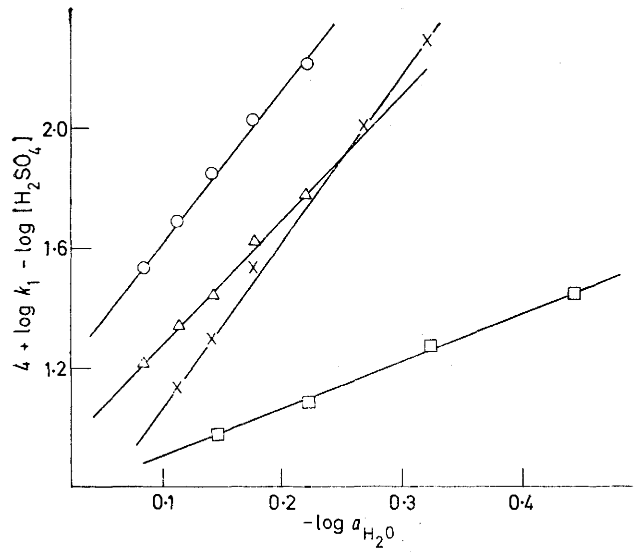

FIGURE 1 Bunnett plots at 30° in sulphuric acid media for oxidation of: ○, glycine; □, DL-alanine; △, DL-valine; ×, DL-leucine

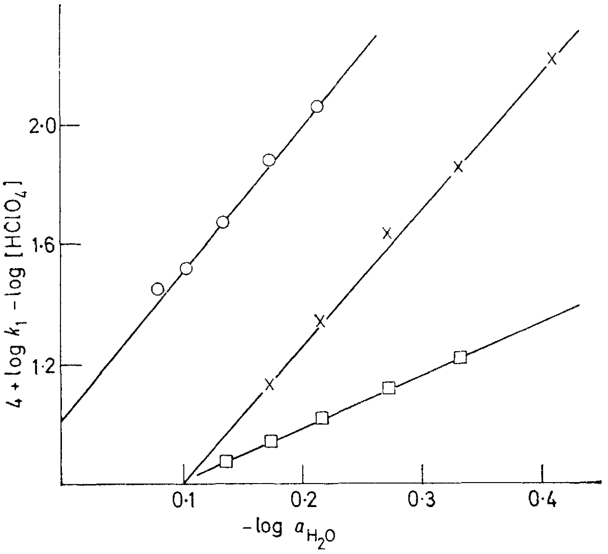

FIGURE 2 Bunnett plots at 30° in perchloric acid media for oxidation of: ○, glycine; □, DL-alanine; ×, DL-leucine

TABLE 5

Thermodynamic parameters for amino-acids at 30°

[Acid] 4.0M; [$KMnO_4$] 10^{-3}M

Amino-acid	ΔE/ kcal/mol^{-1}	ΔS/ cal mol^{-1} K^{-1}	PZ/ l mol^{-1} min^{-1}
Glycine (0.2M)			
10^3k_1/min^{-1} (H_2SO_4)	10.94	−30.80	1.11 × 10^6
10^3k_1/min^{-1} ($HClO_4$)	12.09	−27.81	5.02 × 10^6
DL-Alanine (0.2M)			
10^3k_1/min^{-1} (H_2SO_4)	18.92	−6.85	19.89 × 10^{10}
10^3k_1/min^{-1} ($HClO_4$)	17.33	−12.71	1.03 × 10^{10}
DL-Valine (0.2M)			
10^3k_1/min^{-1} (H_2SO_4)	12.77	−25.19	1.90 × 10^7
DL-Leucine (0.01M)			
10^3k_1/min^{-1} (H_2SO_4)	17.33	−6.21	2.75 × 10^{10}
10^3k_1/min^{-1} ($HClO_4$)	22.80	+5.41	9.69 × 10^{13}

Neutral Salt Effects and Effect of Ionic Strength.—No primary kinetic salt effect was observed by adding neutral salts within the concentration limits demanded for the application of Brønsted–Bjerrum equation. At higher concentrations of added neutral salts the logarithm of the rate constant is linearly related to the ionic strength. This is in accord with equation (3)

$$\log k_1 = \log k_0 + (b_0 + b_a - b^*)\mu \qquad (3)$$

proposed for the higher concentration ranges of the added neutral salts.[20] b_0, b_a, and b^* are constants and are largely empirical. This relationship was found to be true for a number of salts in the case of oxidation of the amino-acids by potassium permanganate. The results for a few salts are given in Figure 3.

The linear plots of log k_1 against μ (Figure 3) show that equation (3) is fairly applicable in the present case, and that the reaction involves two neutral molecules or a neutral molecule and an ion[20] in the rate-determining stage. The positive salt effect further indicates that the reaction is between a positive ion and a molecule.[21]

---

[18] M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1.

[19] J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956.

[20] A. A. Frost and R. G. Pearson, ' Kinetics and Mechanism,' Wiley, New York, 1965, pp. 151—152.

[21] A. K. Wadhawan, P. S. Sankhla, and R. N. Mehrotra, *Indian J. Chem.*, 1973, **11**, 567.

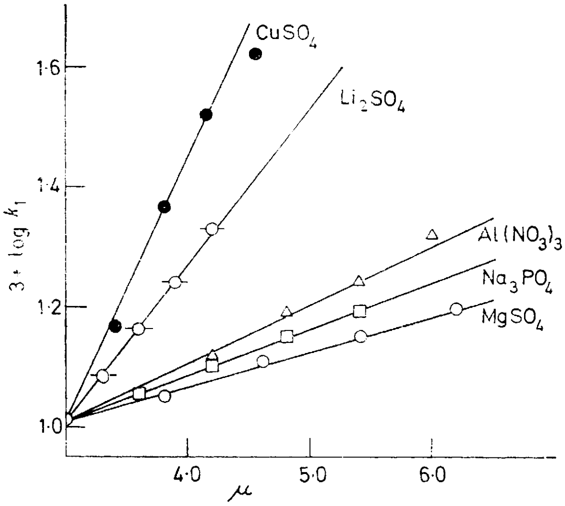

FIGURE 3 Plot of ionic strength against log k, at 30°: [glycine] 0.4M; [H_2SO_4] 3.0M; [$KMnO_4$] 10^{-3}M

Specific Ionic Effects.—If the reactive molecular species or activated complex formed are either charged or dipolar in nature, a specific influence of added cations and anions on the reaction velocity may be expected, depending upon their charge, size, complexing tendency, and general nature. In order to investigate the specific effect of cations and anions on the reaction velocity, therefore, sodium salts of anions and sulphates of cations were added at identical concentrations. Results in the case of oxidation of glycine in sulphuric acid are given in Tables 6 and 7.

TABLE 6

Specific effect of anions at 30°

[Glycine] 0.4M; [H_2SO_4] 3.0M; [$KMnO_4$] 10^{-3}M; [Anion] 0.4M

Anions		$Ch_3CO_2^-$	NO_3^-	ClO_4^-	HSO_4^-	SO_4^{2-}	PO_4^{3-}
10^3k_1/min^{-1}	10.28	8.64	11.46	13.08	13.73	11.02	15.42

TABLE 7

Specific effect of cations at 30°

[Glycine] 0.4M; [H_2SO_4] 3.0M; [$KMnO_4$] 10^{-3}M; [Cation] 0.4M

Cations		Li^+	Na^+	K^+	Cs^+	NH_4^+	Be^{2+}	Mg^{2+}	Cu^{2+}
10^3k_1/min^{-1}	10.28	17.46	11.02	10.01	21.33	12.05	21.51	13.09	41.74
Cations	Ni^{2+}	Zn^{2+}	Cd^{2+}	Al^{3+}	Fe^{3+}				
10^3k_1/min^{-1}	11.15	62.48	12.51	17.21	32.52				

Tables 6 and 7 show that anions and cations do exert specific effects on the reaction velocity supporting the proposed mechanism. The order of effectiveness of the anions is $PO_4^{3-} > HSO_4^- > ClO_4^- > NO_3^- > SO_4^{2-} > CH_3CO_2^-$, for univalent cations $Cs^+ > Li^+ > NH_4^+ > Na^+ > K^+$, for bivalent ions $Zn^{2+} > Cu^{2+} > Be^{2+} > Cd^{2+} > Mg^{2+} > Ni^{2+}$, and for trivalent ions $Fe^{3+} > Al^{3+}$. The overall series for specific effects of cations is $Zn^{2+} > Cu^{2+} > Fe^{3+} > Be^{2+} > Cs^+ > Li^+ > Al^{3+} > Cd^{2+} > Mg^{2+} > NH_4^+ > Ni^{2+} > Na^+ > K^+$.

A critical literature survey on salt and specific ionic effects shows that a generalised theory of the influence of salts on reaction velocity is not yet available. Mishra and Gupta[22] and other workers[23-26] have interpreted specific effects of anions and cations in terms of bridging which facilitates or retards electron transfer in redox systems, while Wahl[27] and his co-workers have interpreted specific effects in terms of complex formation. The present results suggest that specific effects of anions and cations do exist.

Catalysis by Mn^{II} *and* Ag^{I}.—The effect of Mn^{II} as catalyst in case of oxidation by permanganate is well known.[28-31] In the present case Mn^{II} was found to catalyse the rate of oxidation of the amino-acids (Table 8). The catalytic effect of Mn^{II} can be interpreted in either of the two ways. (i) Mn^{II} may form a complex with the amino-acid which is then oxidised by $HMnO_4$ or (ii) Mn^{II} first reacts with Mn^{VII} to produce Mn^{III} which accelerates the rate of the reaction.

TABLE 8

Catalytic effect of Mn^{II} at 30°

[Glycine] 0.4M; [Acid] 3.0M; [$KMnO_4$] 10^{-3}M

$10^4[MnSO_4]$/M	0.0	2.0	4.0	6.0	8.0	10.0
10^3k_1/min^{-1} (H_2SO_4)	10.28	14.46	18.37	22.73	26.26	30.66
10^3k_1/min^{-1} ($HClO_4$)	8.80	11.05	13.54	16.08	18.81	21.84

TABLE 9

Catalytic effect of Ag(^{I}) at 30°

Glycine = 0.4M; [Acid] = 3.0M; [$KMnO_4$] = 10 × 10^{-4}M

$10^3[AgNO_3]$ (M)	0.0	5.0	10.0	15.0	20.0
10^3k_1/min^{-1} (H_2SO_4)	10.28	14.74	18.10	20.41	22.69

---

[22] S. K. Mishra and Y. K. Gupta, *J. Inorg. Nuclear Chem.*, 1968, **30**, 2991.

[23] D. J. Meiler and C. S. Garmer, *J. Phys. Chem.*, 1952, **56**, 853.

[24] F. R. Duke and R. F. Parchen, *J. Amer. Chem. Soc.*, 1956, **78**, 1540.

[25] H. Taube, H. Myers, and R. L. Rich, *J. Amer. Chem. Soc.*, 1953, **75**, 4118.

[26] H. Taube and H. Myers, *J. Amer. Chem. Soc.*, 1954, **76**, 2103.

[27] J. C. Sheppard and A. C. Wahl, *J. Amer. Chem. Soc.*, 1957, **79**, 1020; L. Gjertstn and A. C. Wahl, *ibid.*, 1959, **81**, 1572; A. C. Wahl, *Z. Electrochem.*, 1960, **64**, 90.

[28] J. M. Malcolm and R. M. Noyes, *J. Amer. Chem. Soc.*, 1952, **74**, 2769.

[29] P. Nath, K. K. Banerji, and G. V. Bakore, *J. Indian Chem. Soc.*, 1971, **48**, 17.

[30] M. J. Polissar, *J. Amer. Chem. Soc.*, 1936, **58**, 1372.

[31] G. R. Waterbury, A. M. Hayes, and D. S. Martin, *J. Amer. Chem. Soc.*, 1952, **74**, 15.

Ag^{I} also exhibits a catalytic effect on the reaction (Table 9). It has also been found to catalyse the rate of oxidation of hydrogen by permanganate.[4c]

Mechanism.—The mechanism (4)—(9) is in accord with the results and leads to the rate expression (10)

$$\overset{+}{N}H_3CHRCO_2^- + H^+ \overset{K_1}{\rightleftharpoons} \overset{+}{N}H_3CHRCO_2H \tag{4}$$

$$MnO_4^- + H^+ \overset{K_2}{\rightleftharpoons} HMnO_4 \tag{5}$$

$$\overset{+}{N}H_3CHRCO_2H + HMnO_4 + H_2O \xrightarrow[\text{slow}]{k_1} \overset{+}{N}H_3CHRCO_2^{\cdot} + HMnO_4^- + H_3O^+ \tag{6}$$

$$\overset{+}{N}H_3CHRCO_2^{\cdot} \xrightarrow{\text{fast}} \overset{+}{N}H_3\dot{C}HR + CO_2 \tag{7}$$

$$\overset{+}{N}H_3\dot{C}HR + HMnO_4 \xrightarrow{\text{fast}} \overset{+}{N}H_2{=}CHR + H^+ + HMnO_4^- \tag{8}$$

$$\overset{+}{N}H_2{=}CHR + H_2O \xrightarrow{\text{fast}} RCHO + NH_3 + H^+ \tag{9}$$

$$-d[MnO_4^-]/dt = k[\text{Amino acid}][MnO_4^-] \tag{10}$$

at a given concentration of acid, with k given by equation (11).

$$k = k_1K_1K_2[H^+]^2[H_2O]/(1 + K_2[H^+]) \tag{11}$$

Similar mechanisms for one equivalent oxidative decarboxylations have been proposed by many workers.[15,32–34] Step (8) resembles that proposed by Rosenblatt and his co-workers.[35,*]

The induced reduction of mercury(II) chloride[36] by the permanganate–amino-acid system in moderately concentrated acidic (sulphuric and perchloric) media confirms that the free radicals responsible for the reduction of Hg^{2+} ions are produced in this system.

The proposed mechanism is further supported by analysis of the products. Ammonia has been detected as ammonium ions in solution for all four amino-acids. Formaldehyde,[37a] acetaldehyde,[37b] isobutyraldehyde,[37c] and isovaleraldehyde[37c] were detected as the oxidation product from the appropriate amino-acid. Similar products using different oxidants have been suggested by Barkat and his co-workers,[38] Kumar and Saxena,[7] and by Govind Chandra.[8]

The rates of oxidation of amino-acids in moderately concentrated sulphuric and perchloric acid by potassium permanganate are in the order DL-leucine > glycine > DL-valine > DL-alanine. The order of the relative reactivities of the amino-acids is in accord with the views of Pokrovskaya[5] who observed that amino-acids with an even number of atoms in the carbon chain are more easily oxidized in acidic media than those with an odd number of atoms.

It is also interesting to observe that the order of the magnitudes of the activation parameters is also consistent with Pokrovskaya's odd–even effect.[5] This effect arises from several causes such as the structure of the given zwitterion, the effect of the side chain in the molecule, *etc.*

We thank Professor M. M. Bokadia for his interest. One of us (R. S. V.) is grateful to the C.S.I.R., New Delhi, India, for the award of a Junior Research Fellowship.

[5/1402 *Received, 16th July, 1975*]

---

[*] We thank a referee for suggesting this step.

[32] J. M. Anderson and J. K. Kochi, *J. Chem. Soc.*, 1970, **92**, 1651.

[33] R. N. Mehrotra, *J. Chem. Soc.* (*B*), 1968, 1563.

[34] N. C. Khandual and P. L. Nayak, *J. Indian Chem. Soc.*, 1973, **50**, 194.

[35] D. H. Rosenblatt, G. T. Davis, L. A. Hull, and G. D. Forberg, *J. Org. Chem.*, 1968, **33**, 1649.

[36] A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, 1953, 2836, 3119.

[37] F. Feigl, 'Spot Tests in Organic Chemistry,' Elsevier, Amsterdam, 1956 (*a*) p. 331; (*b*) p. 335; (*c*) p. 351.

[38] M. Z. Barkat, M. F. Abdel Wahab, and M. M. Elsadag, *J. Chem. Soc.*, 1956, 4685.