

Mechanism of Redox Reactions in Partially Aqueous Medium: Kinetics of Oxidation of Amino Acids by Dichloramine-T

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The kinetics of oxidation of amino acids, namely, glycine, alanine, valine, leucine and serine by dichloramine-T (DCT) has been investigated in 50% (v/v) aqueous acetic acid and 50% (v/v) aqueous methanol media. In both the media the reaction shows second order dependence in [DCT]. In the presence of acetate ions, in aqueous acetic acid, the reaction is zero order in [amino acid] and negligible inverse fractional order in added [HClO₄]. The rate increases with increase in ionic strength of the medium and with increase in [acetate] at constant ionic strength with a fractional order dependence in [acetate], indicating the participation of acetate ions in the reaction. In aqueous methanol or acetic acid medium, in the absence of acetate ions, the rate shows fractional order dependence in [amino acid] and inverse fractional order in [H⁺]. Effects of changes in solvent composition and the reaction product on the rate have also been investigated in all cases. Activation parameters have been computed from the Arrhenius plots in both the media. Suitable mechanistic schemes in conformity with the observed kinetics have been suggested.

Extensive works have been reported from our laboratories¹⁻⁹ on the kinetics and mechanism of oxidation of a variety of organic substrates by N-halo-N-metallo sulphonamides like chloramine-T, bromamine-B and bromamine-T. However, similar studies on the kinetics of oxidation of organic substrates by dihalosulphonamides like dichloramine-T or dibromamine-T do not appear to have been carried out so far and hence the need for the title investigation.

Materials and Methods

Dichloramine-T (DCT) was prepared in the laboratory and its purity was checked by elemental analyses, iodometric estimation of the active halogen present in it, IR and NMR spectral data. A stock solution of the compound ($\sim 0.05 \text{ mol dm}^{-3}$) in water-free acetic acid or methanol was prepared, standardised by the iodometric method and preserved in dark coloured bottles. Chromatographically pure amino acids, namely, L-glycine (Gly), L-alanine (Ala), L-valine (Val), L-leucine (Leu) and L-serine (Ser) were used. All other reagents used were of AR grade. The ionic strength of the medium was kept at a high value by adding sodium acetate (0.2 mol dm^{-3}) and sodium perchlorate (0.4 mol dm^{-3}) in aqueous acetic acid and sodium perchlorate (0.4 mol dm^{-3}) in aqueous methanol.

Kinetic Measurements

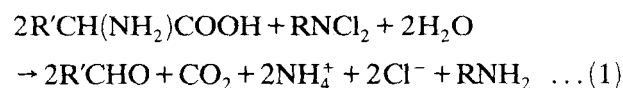
The reactions were carried out in 50% (v/v) aqueous acetic acid or 50% (v/v) aqueous methanol under pseudo-second order conditions, ([amino ac-

id] \gg [DCT]) in pyrex tubes coated black outside. The reactions were initiated by the quick addition of a measured quantity of DCT solution (in acetic acid or methanol), thermally equilibrated at a desired temperature, to a mixture containing appropriate amounts of amino acid solution, HClO₄, sodium acetate (or sodium perchlorate), acetic acid (or methanol) and water [to maintain 50% (v/v) solvent composition], equilibrated at the same temperature. The progress of the reaction was monitored for nearly two half-lives by estimating the unreacted DCT iodometrically at regular time intervals. Clean kinetics were observed up to 70% completion of the reaction. The pseudo-second order rate constants computed by the method of least squares were reproducible within $\pm 6\%$.

Stoichiometry

The stoichiometry of DCT-amino acid reaction was determined under varying experimental conditions and the products was identified as the corresponding aldehyde by conventional tests. *p*-Toluenesulphonamide (PTS), the reduced product of DCT, was detected by paper chromatography.

The observed stoichiometry may be represented by Eq. (1).



where R = CH₃C₆H₄SO₂, R' = H (Gly), CH₃ (Ala), (CH₃)₂CH (Val), (CH₃)₂CHCH₂ (Leu) and HOCH₂ (Ser).

Results

The kinetics of oxidations were investigated at several initial concentrations of DCT, amino acids and H^+ in 50% (v/v) aqueous acetic acid, both in the presence and absence of added acetate ions and in 50% (v/v) aqueous methanol and the results are shown in Tables 1-5.

(a) Reaction in 50% (v/v) aqueous acetic acid: (i) In the presence of added acetate ions

The rate was unaffected by the change in [amino acid]. Variation in $[H^+]$ by adding $HClO_4$ had little effect on the rate of oxidation (Table 3). Plots of $\log k_{obs}$ versus $\log [HClO_4]$ showed negligible fractional inverse order in $[H^+]$ (~ 0.2). The behaviour of perchloric acid was quite unusual. Twenty-fold variation in $[HClO_4]$ resulted in little change in pH (~ 0.5 units only) (Table 3). Plots of $\log k_{obs}$ versus pH were also linear with varying fractional slopes (Table 5). Increase in ionic strength of the medium by adding sodium acetate increased the rate in all the cases (Table 3) and the plots of $\log k_{obs}$ versus $\sqrt{\mu}$ were linear. This was also verified by investigating the effect of varying [acetate] at a fixed ionic strength (Table 3). pH of the reaction mixtures were measured with change in [acetate]. The plots of $\log k_{obs}$ versus pH (or $\log [H^+]$) were linear, with varying fractional slopes (Table 5). The plots of k_{obs} versus $[NaOAc]$ were also linear with intercepts on the ordinate indicating the participation of acetate ions in the reaction, i.e. the effect of acetate on the rate is not only due to secondary salt effect but also due to its participation.

(ii) In the absence of added acetate ions

In the absence of added acetate ions, the rate was slow and dependent on [amino acid] (Table 2). The rate showed second order dependence in [DCT], fractional order in [amino acid] and inverse fractional order in $[H^+]$.

(b) Reactions in 50% (v/v) aqueous methanol

The reaction was second order in [DCT] in this solvent also. The rates increased with increase in [amino acid] and the plots of $\log k_{obs}$ versus $\log [amino\ acid]$ were linear with fractional slopes, showing fractional order dependence in [amino acid]. The rates decreased with increase in $[H^+]$ for all the amino acids (Table 4) and the plots of $\log k_{obs}$ versus pH were linear with fractional slopes, showing inverse fractional order dependence in $[H^+]$. Variation of ionic strength of the medium using concentrated solution of $NaClO_4$ had negligible effects on the rates.

Addition of the reaction product, *p*-toluenesulphonamide had no effect on the reaction rates in both the media for all the amino acids. The rate decreased

Table 1—Pseudo-second Order Rate Constants (k_{obs}) for Oxidation of Amino Acids by DCT.

[Solvent: Aq. acetic acid (50% v/v); temp = 308 K; $\mu = 0.2$ mol dm⁻³ (NaOAc).]

10 ³ [DCT] (mol dm ⁻³)	10 ² [AA] (mol dm ⁻³)	10 k_{obs} (dm ³ mol ⁻¹ s ⁻¹)		
		Ala	Val	Leu
0.50	1.0	—	1.9	1.9
0.75	1.0	2.3	—	—
1.0	1.0	2.2	1.9	1.8
2.0	1.0	2.1	1.9	1.8
5.0	1.0	1.9	1.8	1.7
1.0	0.5	2.2	2.0	1.7
1.0	1.0	2.2	1.8	1.9
1.0	2.0	2.2	1.7	1.8
1.0	5.0	2.7	1.6	1.8
1.0 ^{a1}	1.0	2.1	1.9	1.7
1.0 ^{a2}	1.0	2.0	1.8	1.6
1.0 ^{b1}	1.0	0.9	1.0	0.7
1.0 ^{b2}	1.0	1.2	1.4	1.1
1.0 ^{b3}	1.0	2.9	2.4	2.3
1.0 ^{c1}	1.0	17.6	9.4	13.3
1.0 ^{c2}	1.0	9.1	5.4	6.2
1.0 ^{c3}	1.0	0.7	0.8	0.6

^a In presence of PTS, 10³[PTS] (mol dm⁻³) = (1) 2.0, (2) 5.0.

^b With ionic strength, [NaOAc] (mol dm⁻³) = (1) 0.05, (2) 0.1, (3) 0.3.

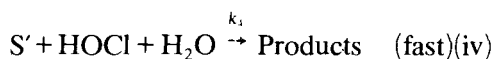
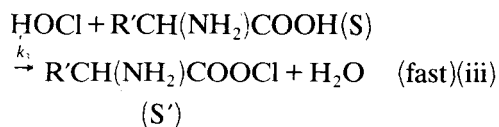
^c With solvent composition; HOAc (% v/v) = (1) 20, (2) 30, (3) 70.

with decrease in dielectric constant of the medium in both the media (Tables 1 and 2). The reaction rates were measured at different temperatures (293-318 K) and the activation parameters were computed from the Arrhenius plots.

Discussion

(1) Mechanism of oxidation in aqueous acetic acid in the presence of added acetate ions

The observed kinetics for oxidation of amino acids by DCT, in aqueous acetic acid medium, can be explained by the mechanism shown in Scheme 1. Formation of acyl hypochlorite (step-iii) is supported by the observation recorded in literature¹⁰.



Scheme 1

Table 2—Pseudo-second Order Rate Constants (k_{obs}) for the Oxidation of Amino Acids by DCT.

[Solvents: Aq. acetic acid, aq. methanol (50% v/v); $\mu = 0.4 \text{ mol dm}^{-3}$ (NaClO_4).

$10^3[\text{DCT}]$ (mol dm^{-3})	$10^2[\text{AA}]$ (mol dm^{-3})	$10 k_{obs}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) in 50% aq. AcOH at 313 K				$10^3[\text{DCT}]$ (mol dm^{-3})	$10^2[\text{AA}]$ (mol dm^{-3})	$10 k_{obs}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$) in 50% aq. MeOH at 308 K	
		Ala	Val	Leu ^d	Ser ^e			Gly	Val
1.0	5.0	1.0	1.0	0.57	—	4.0	5.0	1.7	1.1
2.0	5.0	1.0	1.0	0.51	0.73	5.0	5.0	1.5	1.0
4.0	5.0	0.9	0.9	0.54	0.76	8.0	5.0	1.5	1.2
5.0	5.0	0.9	0.8	0.54	0.76	5.0	1.0	0.4	0.3
10.0	5.0	—	0.8	—	0.77	5.0	2.0	0.7	0.5
2.0	1.0	0.3	0.4	0.36	0.35	5.0	7.5	2.0	1.5
2.0	2.0	0.5	0.5	0.51	0.44	5.0	10.0	2.8	—
2.0	3.0	—	—	0.70	—	5.0 ^{a1}	5.0	1.5	1.1
2.0	4.0	—	—	0.83	—	5.0 ^{a2}	5.0	1.5	1.1
2.0	6.0	—	—	1.10	—	5.0 ^{a3}	5.0	1.4	1.2
2.0	7.5	1.5	1.4	—	1.00	5.0 ^{b1}	5.0	1.2	1.0
2.0	10.0	1.8	—	—	1.20	5.0 ^{b2}	5.0	1.6	1.0
2.0 ^{a1}	5.0	0.9	1.0	0.50	0.76	5.0 ^{c1}	5.0	1.9	3.7
2.0 ^{a2}	5.0	0.9	0.9	0.48	0.73	5.0 ^{c2}	5.0	1.6	2.7
2.0 ^{a3}	5.0	0.9	0.9	0.46	0.73	5.0 ^{c3}	5.0	1.2	0.8
2.0 ^{b1}	5.0	1.0	1.1	0.53	0.75				
2.0 ^{b2}	5.0	1.0	1.1	0.49	0.74				
2.0 ^{c1}	5.0	6.8	4.2	3.20	4.30				
2.0 ^{c2}	5.0	3.7	2.6	1.70	2.40				
2.0 ^{c4}	5.0	0.4	0.3	0.26	0.30				

^a In the presence of PTS, $10^3[\text{PTS}]$ (mol dm^{-3}) = (1) 2.0, (2) 5.0, (3) 10.0.

^b With ionic strength, μ (mol dm^{-3}) = (1) 0.2, (2) 0.5.

^c With solvent composition; HOAc (% v/v) = (1) 20, (2) 30, (3) 60, (4) 70.

^d $[\text{Leu}] = 0.02 \text{ mol dm}^{-3}$ except while varying $[\text{Leu}]$.

^e $[\text{DCT}] = 0.004 \text{ mol dm}^{-3}$ except while varying $[\text{DCT}]$.

Table 3—Effect of $[\text{HClO}_4]$ and $[\text{NaOAc}]$ on Rate of Oxidation of Amino Acids by DCT in Aqueous Acetic Acid (50% v/v)

$10^2[\text{HClO}_4]^a$ (mol dm^{-3})	pH	$10 k_{obs}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)					
		Ala	Val	Leu	Ala	Val	Leu
0.5	2.56	2.55	2.46	2.2	1.9	1.6	
1.0	2.49	2.50	2.43	2.0	1.7	1.5	
5.0	2.31	2.33	2.29	1.7	1.5	1.3	
10.0	2.06	2.14	2.09	1.3	1.2	1.0	
$10[\text{NaOAc}]^b$	Ala	Val	Ser	Ala	Val	Ser	
0.5	2.00	2.00	1.85	2.0	1.4	1.2	
1.0	2.22	2.17	2.10	2.7	1.8	1.9	
2.0	2.52	2.47	2.40	4.0	2.6	3.5	
3.0	3.00	2.77	2.55	5.4	3.5	5.1	

^a $[\text{DCT}]_0$ (mol dm^{-3}) = 0.001, $[\text{AA}]$ (mol dm^{-3}) = 0.01, $\mu = 0.2 \text{ mol dm}^{-3}$ with added NaOAc, temp = 308 K.

^b $[\text{DCT}]_0$ (mol dm^{-3}) = 0.002, $[\text{AA}]$ (mol dm^{-3}) = 0.05, $\mu = 0.4 \text{ mol dm}^{-3}$ with added NaClO_4 , temp = 313 K.

Scheme 1 leads to rate law (2)

$$-\frac{d[\text{DCT}]}{dt} = k_1[\text{DCT}]_0^2[\text{H}_2\text{O}]^2$$

or

$$-\frac{d[\text{DCT}]}{dt} = k'_1[\text{DCT}]_0^2 \quad \text{where } k'_1 = k_1[\text{H}_2\text{O}]^2 \quad \dots (2)$$

The dependence of rate on $[\text{HClO}_4]$ (or $[\text{H}^+]$) may be due to a fraction of reaction going through an alternate path (Scheme 2).

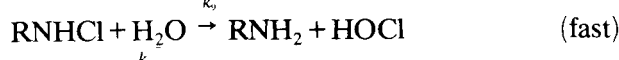
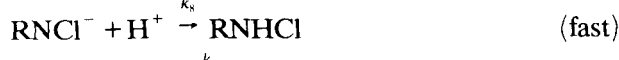
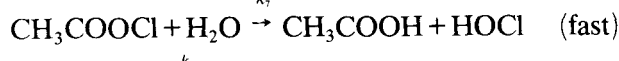
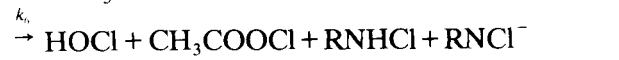
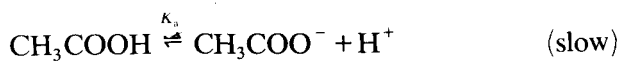


Table 4—Effect of $[\text{HClO}_4]$ on Rate of Oxidation of Amino Acids by DCT in 50% (v/v) Aqueous Acetic Acid and Aqueous Methanol.

($\mu = 0.4 \text{ mol dm}^{-3}$ with NaClO_4)

$10^2[\text{HClO}_4]$ (mol dm^{-3})	pH				$10k_{\text{obs}}$ ($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$)				pH		$10k_{\text{obs}}$ ($\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$)	
	Ala	Val	Leu	Ser	Ala	Val	Leu	Ser	Gly	Val	Gly	Val
	Solvent: 50% aq. AcOH; temp = 313 K ^a								Solvent: 50% aq. MeOH; temp = 308 K ^b			
0.5	1.54	1.63	1.35	1.56	0.9	0.9	0.5	0.7	3.35	3.05	1.8	1.2
1.0	1.42	1.54	1.25	1.50	0.8	0.8	0.4	0.6	3.24	2.83	1.5	1.0
2.0	1.30	1.33	1.03	1.40	0.6	0.6	0.3	0.5	—	—	—	—
3.0	—	—	0.86	1.26	—	—	0.2	0.4	—	2.50	—	0.8
5.0	0.90	1.11	—	—	0.4	0.5	—	—	2.09	1.56	0.3	0.6
10.0	—	—	—	—	—	—	—	—	1.31	—	0.2	—

^a $[\text{DCT}]_0$ (mol dm^{-3}) = 0.002 (Ala, Val, Leu) and 0.004 (Ser), $[\text{AA}]_0$ (mol dm^{-3}) = 0.05 (Ala, Val, Ser) and 0.02 (Leu).

^b $[\text{DCT}]_0$ (mol dm^{-3}) = 0.005; $[\text{AA}]_0$ (mol dm^{-3}) = 0.05.

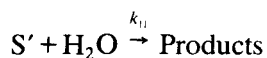
Table 5—Kinetic Data and Activation Parameters for the Oxidation of Amino Acids by DCT in Aqueous Acetic Acid and Aqueous Methanol.

[Values represent order of reaction in respect of variable in column 1]

Ordered observed in	50% (v/v) aq. AcOH with added NaOAc			50% (v/v) aq. AcOH with added NaClO_4			50% (v/v) aq. MeOH		
	Ala	Val	Leu	Ala	Val	Leu	Ser	Gly	Val
$[\text{DCT}]_0$	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
$[\text{AA}]_0$	0	0	0	0.8	0.7	0.6	0.6	0.9	0.6
$[\text{H}^+]_{\text{eff}}^{\text{a}}$	-0.5	-0.8	-0.7	-0.5	-0.6	-0.4	-0.7	-0.6	-0.8
$[\text{CH}_3\text{COO}^-]$	0.6	0.7	0.4	0.6	0.4	—	0.8	—	—
$[\text{H}^+]_{\text{eff}}^{\text{b}}$	-0.5	-0.5	-0.5	-0.5	-0.3	—	-0.4	—	—
Parameter									
Log A	10.1	9.8	9.3	9.3	9.0	8.2	9.0	9.5	10.3
E_a , kJ mol^{-1}	62.3	61.9	58.9	61.6	60.0	56.7	60.5	60.9	66.4
ΔH^\ddagger , kJ mol^{-1}	60.8	59.4	56.4	59.0	57.4	54.2	58.0	58.3	63.9
ΔS^\ddagger , JK^{-1}	-59.5	-65.8	-74.8	-75.7	-81.0	-97.3	-81.9	-72.3	-56.2
ΔG^\ddagger , kJ mol^{-1}	79.1	79.6	79.4	82.7	82.8	84.6	83.6	80.6	81.2

^a Calculated from the measured pH values as $[\text{HClO}_4]$ varied.

^b Calculated from the measured pH values as $[\text{NaOAc}]$ varied.



Scheme 2

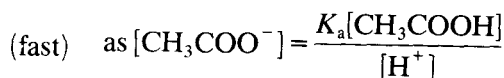
Scheme 2 leads to rate law (3).

$$\begin{aligned} -\frac{d[\text{DCT}]}{dt} &= K_5 k_6 [\text{DCT}]_0^2 [\text{CH}_3\text{COO}^-] [\text{H}_2\text{O}] \\ &= K_5 k_6' [\text{DCT}]_0^2 [\text{CH}_3\text{COO}^-] \quad \dots (3) \end{aligned}$$

where $k_6' = k_6 [\text{H}_2\text{O}]$.

or

$$-\frac{d[\text{DCT}]}{dt} = K_a K_5 k_6 [\text{DCT}]_0^2 \frac{[\text{CH}_3\text{COOH}]}{[\text{H}^+]},$$



or

$$-\frac{d[\text{DCT}]}{dt} = K_5 k_6'' \frac{[\text{DCT}]_0^2}{[\text{H}^+]}$$

$$\text{where } k_6'' = K_a k_6 [\text{CH}_3\text{COOH}] \quad \dots (4)$$

The observed results (Table 5) can be explained by the combined rate law (5).

$$-\frac{d[\text{DCT}]}{dt} = k_1 [\text{DCT}]_0 + K_5 k_6'' \frac{[\text{DCT}]_0^2}{[\text{H}^+]}$$

or

$$k_{\text{obs}} = k_1 + K_5 k_6'' \frac{1}{[\text{H}^+]} \quad \dots (5)$$

Table 6—Comparison of Calculated and Observed Rate Constants

(Solvent: Aq. acetic acid (50% v/v); temp = 308 K.)

$10^2[\text{HClO}_4]$ (mol dm ⁻³)	$10 k_{\text{obs}}^{\text{a,b}}$ (dm ³ mol ⁻¹ s ⁻¹)		
	Ala	Val	Leu
0.5	2.3(1.8)	1.9(2.1)	1.6(1.5)
1.0	2.0(1.6)	1.7(1.9)	1.5(1.5)
5.0	1.8(1.3)	1.5(1.5)	1.3(1.2)
10.0	1.3(1.0)	1.2(1.2)	1.0(0.9)

$10[\text{NaOAc}]$ (mol dm ⁻³)	$10 k_{\text{obs}}^{\text{a,b}}$ (dm ³ mol ⁻¹ s ⁻¹)		
	Ala	Val	Leu
0.5	0.9(1.1)	1.0(1.1)	0.7(0.8)
1.0	1.2(1.5)	1.4(1.4)	1.1(1.1)
2.0	2.2(2.8)	1.9(2.1)	1.8(1.7)
3.0	2.9(3.6)	2.5(2.5)	2.2(2.3)

^a $10^3[\text{DCT}]_0 = 1.0 \text{ mol dm}^{-3}$, $10^2[\text{AA}] = 1.0 \text{ mol dm}^{-3}$, $\mu = 0.2 \text{ mol dm}^{-3}$ with added $[\text{NaOAc}]$ while varying $[\text{HClO}_4]$.

^b Calculated values in parentheses.

For the variation of $[\text{CH}_3\text{COO}^-]$, rate law (6) is applicable.

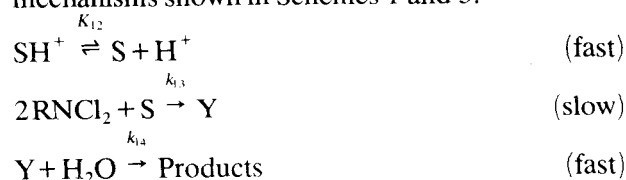
$$k_{\text{obs}} = k_1' + K_5 k_6 [\text{CH}_3\text{COO}^-] \quad \dots (6)$$

The linear plots of k_{obs} versus $1/[\text{H}^+]$ (Fig. 1) in the presence of different concentrations of acetate or HClO_4 and of k_{obs} versus $[\text{acetate}]$ (Fig. 2) support the combined rate laws (5) and (6) and confirm the participation of acetate directly in the reaction, in addition to its secondary salt effect. This has been verified by investigating the effect of acetate ions at a fixed ionic strength (Table 3).

The constants computed from the plots of k_{obs} versus $1/[\text{H}^+]_{\text{eff}}$ for the variation of acetate were used to predict the rate constants, from rate law (5) for the variation of $[\text{H}^+]_{\text{eff}}$, while $[\text{HClO}_4]$ was varied and vice versa. The predicted values compared favourably with the experimental values (Table 6) thereby supporting the validity of the reaction schemes.

Mechanisms of oxidation in (i) aqueous acetic acid in the absence of added acetate and (ii) aqueous methanol

The second order in $[\text{DCT}]$, fractional order in $[\text{amino acid}]$ and inverse fractional order in $[\text{H}^+]$ under above experimental conditions may be explained by mechanisms shown in Schemes 1 and 3.



Scheme 3

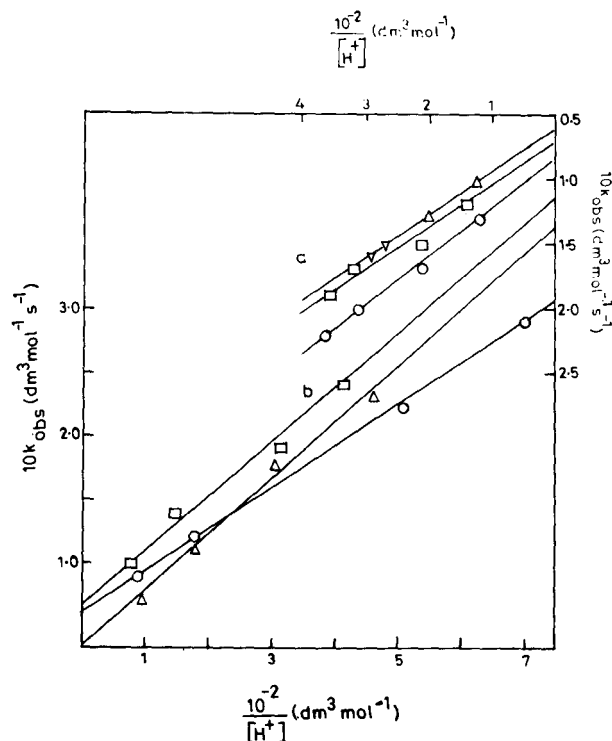


Fig. 1—(a) k_{obs} versus $1/[\text{H}^+]$ at different $[\text{NaOAc}]$ [\circ Ala, \square Val, \triangle Leu] (b) k_{obs} versus $1/[\text{H}^+]$ at different $[\text{HClO}_4]$ ($\mu = 0.2 \text{ mol dm}^{-3}$) [\circ Ala, \square Val, \triangle Leu] $10^3 [\text{DCT}] = 10^2 [\text{AA}] = 1.0 \text{ mol dm}^{-3}$; temp = 308 K; medium 50% (v/v) aq. HOAc.

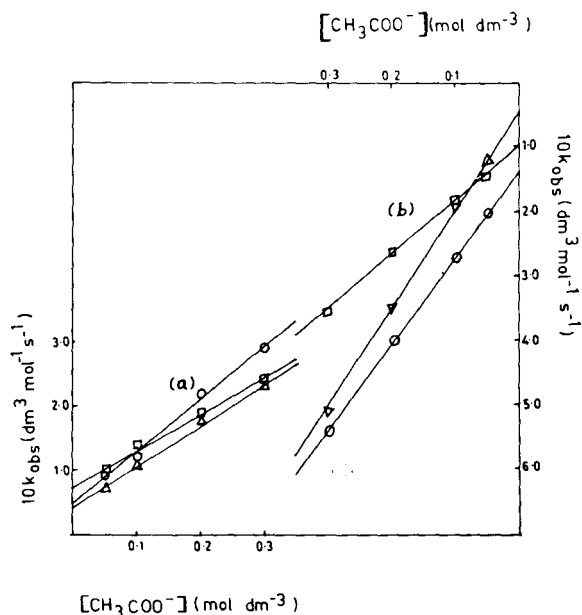


Fig. 2—(a) k_{obs} versus $[\text{acetate}]$ at different ionic strength. [\circ Ala, \square Val, \triangle Leu; $10^3[\text{DCT}] = 10^2[\text{AA}] = 1.0 \text{ mol dm}^{-3}$; temp = 308 K; medium 50% (v/v) aqueous acetic acid], (b) k_{obs} versus $[\text{acetate}]$ at $\mu = 0.4 \text{ mol dm}^{-3}$ with NaClO_4 ; [\circ Ala, \square Val, \triangle Ser; $10^3[\text{DCT}] = 2.0 \text{ mol dm}^{-3}$, $10^2[\text{AA}] = 5.0 \text{ mol dm}^{-3}$; temp = 313 K, medium 50% (v/v) aqueous HOAc.]

Schemes 1 and 3 lead to combined rate law (7)

$$-\frac{d[\text{DCT}]}{dt} = k_1[\text{DCT}]^2[\text{H}_2\text{O}]^2 + k_{13}[\text{DCT}]^2[\text{S}] \quad \dots (7)$$

or

$$k_{\text{obs}} = k_1[\text{H}_2\text{O}]^2 + k_{13}[\text{S}] \\ = k_1[\text{H}_2\text{O}]^2 + K_{12}k_{13} \frac{[\text{SH}^+]}{[\text{H}^+]} \quad \dots (8)$$

The plots of k_{obs} versus [amino acid] and k_{obs} versus $1/[\text{H}^+]$ were linear with finite intercepts in accordance with rate law (8). The constant k_{13} was computed from the slope of the former plot. The values are: k_{13} ($\text{dm}^6\text{mol}^{-2}\text{s}^{-1}$) = 1.8 (Ala), 1.5 (Val), 1.5 (Leu) and 0.9 (Ser) in aqueous HOAc and 2.5 (Gly) and 1.8 (Val) in aqueous methanol.

Decrease in rate with decrease in dielectric constant of the medium, observed in all cases, is in conformity with Amis¹¹ and other theories.

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