

**Kinetics of Oxidation of Aliphatic Amines by Tl(III) in Acetic Acid Medium**

 R. VEDA VRATH, B. SETHURAM & T. NAVANEETH RAO\*  
 Department of Chemistry, Osmania University,  
 Hyderabad 500 007

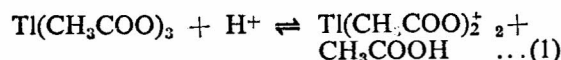
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Kinetics of oxidation of methyl, ethyl, *n*-propyl, *n*-butyl, isobutyl and *n*-hexyl amines by Tl(III) in acetic acid have been investigated. The products of oxidation have been identified as the corresponding aldehyde or ketone and ammonia. The kinetic data and product analysis point to an attack on the free amine. Taft's plot is linear giving a  $\rho^*$  value of  $-5.41$  at  $60^\circ\text{C}$ . A mechanism involving  $\alpha$ -C-H bond rupture is postulated.

THE oxidation of amines by various oxidants like permanganate<sup>1</sup>, lead tetraacetate<sup>2</sup>, cobaltic perchlorate<sup>3</sup>, chlorine dioxide<sup>4</sup> and N-bromosuccinimide<sup>5</sup> have been reported earlier. Two different mechanisms, one involving dehydrogenation<sup>2</sup> and the other simultaneous attack at C-H bond and lone pair on nitrogen<sup>6</sup> by the oxidising agent in the rate determining step have been postulated. The present work has been undertaken with a view to finding out which one of the above two mechanisms is operative in the oxidation of amines when Tl(III) is used as the oxidant.

All the amines used were Riedel samples. To prevent the alteration of acid strength due to protonation of amine, the salts of the amines of the general formula  $\text{RCH}_2\text{NH}_3^+\text{HSO}_4^-$  were prepared by mixing equimolar quantities of amine and sulphuric acid in the cold. Thallous acetate was prepared by the usual method<sup>7</sup>. The products of oxidation were identified as the corresponding aldehyde or ketone and ammonia. Aldehydes and ketones were characterised by preparing their 2, 4-DNP derivatives and comparing their melting points with authentic samples.

Under the conditions of  $[\text{Tl(III)}] \ll [\text{amine}]$ , the reaction exhibited first order dependence on  $[\text{Tl(III)}]$  for all the amines studied. The concentrations of amines used were: [Methyl amine] = 2.5-3.8 M; [Ethyl amine] = 1.0-4.0 M; [*n*-Propyl amine] = 0.94-3.7 M; [*n*-Butyl amine] = 0.5-1.5 M; [Isobutyl amine] = 1.0-3.0 M; [*n*-Hexyl amine] = 0.95-2.8 M;  $[\text{Tl}^{3+}] = 0.001\text{-}0.006\text{ M}$ . The pseudo-first order rate constants ( $k'$ ) were calculated from the slopes of the linear plots,  $\log(a-x)$  versus time. The plots of  $\log k'$  versus  $\log [\text{amine}]$  were linear with unit slope, indicating the order in [amine] also to be unity. With increase in percentage of acetic acid, the rate decreased (Table 1). This may be explained by postulating the equilibrium and assuming  $\text{Tl}(\text{CH}_3\text{COO})_2^+$  to be the reactive species:



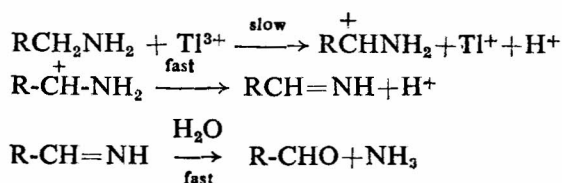
According to Eq. (1) the rate should increase with increase in  $[\text{H}^+]$ . However, in the present work

the rate slightly decreased with increase in  $[\text{H}^+]$  (Table 2). In acid solutions the free amine gets protonated and the equilibrium (2) is likely to be operative.



Equilibria (1) and (2) oppose each other in so far as the effect of  $[\text{H}^+]$  on the rate is concerned; the effect of  $[\text{H}^+]$  on the rate indicates that probably both the equilibria are present and that the reactive species are  $\text{Tl}(\text{CH}_3\text{COO})_2^+$  and  $\text{RCH}_2\text{NH}_2$ .

On the basis of kinetic and non-kinetic evidences the postulated mechanism of oxidation of amine by Tl(III) is shown in Scheme 1.



Scheme 1

The other two alternative modes of attack of  $\text{Tl}^{3+}$  on  $\text{RCH}_2\text{NH}_2$  could be to generate  $\text{RCH}_2\text{NH}^+$  or  $\text{RCH}_2\text{-NH}_2^+$  radical. The radical mechanism was ruled out, since no polymerization of acrylonitrile when added to the reaction system occurred.

If the attack were to be at  $\alpha$ -C-H or N-H, the ions  $\text{RCHNH}_2^+$  or  $\text{RCH}_2\text{NH}^+$  would be produced. Out of these two ions  $\text{RCHNH}_2^+$  is more stable than  $\text{RCH}_2\text{NH}^+$ , since in the carbonium ion intermediate, there are more chances for charge dispersal due to hyperconjugation and inductive effects. Further, nitrogen being more electronegative than carbon,

 TABLE 1 — EFFECT OF VARYING  $[\text{CH}_3\text{COOH}]$  ON  $k'$  IN  $\text{Tl}^{3+}$ -*n*-PROPYL AMINE REACTION

 $[\text{Tl}^{3+}] = 2.5 \times 10^{-3}\text{ M}$ ; [*n*-Propyl amine] = 2.37 M; Temp. = 333 K

$[\text{CH}_3\text{COOH}]$ % (v/v)	$k' \times 10^4$ $\text{dm}^3\text{mol}^{-1}\text{min}^{-1}$	$[\text{CH}_3\text{COOH}]$ % (v/v)	$k' \times 10^4$ $\text{dm}^3\text{mol}^{-1}\text{min}^{-1}$
10.0	16.0	40.0	9.43
25.0	11.7	50.0	7.35

 TABLE 2 — EFFECT OF VARYING  $[\text{H}^+]$  IN  $\text{Tl}^{3+}$ -*n*-PROPYL AMINE REACTION

 $[\text{Tl}^{3+}] = 2.5 \times 10^{-3}\text{ M}$ ; [*n*-Propyl amine] = 2.37 M; acetic acid = 10% (v/v); temp. = 337K.

$[\text{H}_2\text{SO}_4]$ M	$k' \times 10^3$ $\text{min}^{-1}$	$[\text{H}_2\text{SO}_4]$ M	$k' \times 10^3$ $\text{min}^{-1}$
0.460	3.80	1.84	3.40
0.920	3.60	3.68	3.30

TABLE 3 — ACTIVATION PARAMETERS FOR OXIDATION OF AMINES BY TI(III)

Temp. = 333 K; solvent = 10% aq. acetic acid (v/v)

Amine	$k'' \times 10^4$ dm <sup>3</sup> mol <sup>-1</sup> min <sup>-1</sup>	$E_a$	$\Delta H^\ddagger$ k J mol <sup>-1</sup>	$\Delta G^\ddagger$	$-\Delta S^\ddagger$ J deg <sup>-1</sup> mol <sup>-1</sup>
Methyl	0.018	19.3	16.7	118	294
Ethyl	9.00	28.6	26.2	101	223
<i>n</i> -Propyl	16.0	34.6	32.0	99.4	202
Butyl	51.0	39.1	36.5	96.1	178
Isobutyl	66.4	40.3	37.1	95.3	171
<i>n</i> -Hexyl	68.0	41.1	38.6	95.3	169

[Methyl amine] = 3.80M; [Ethyl amine] = 3.00M;  
 [*n*-Propyl amine] = 2.88 M; [Butyl amine] = 1.5 M;  
 [Isobutyl amine] = 2.00 M; [*n*-Hexyl amine] = 2.35 M;  
 [TI<sup>3+</sup>] = 2.5 × 10<sup>-3</sup> M.

removal of hydrogen as H<sup>-</sup> from the carbon is easier. In the light of the above arguments, an attack at  $\alpha$ -CH (Scheme 1) in the rate-determining step, appears reasonable. Such an attack has been suggested in the oxidation of alcohols by TI(III)<sup>8</sup>. The reactivities of amines follow the order methyl < ethyl < *n*-propyl < *n*-butyl < isobutyl < *n*-hexyl. The reactivity order could be explained in terms of increasing inductive effect of the groups attached to  $\alpha$ -CH<sub>2</sub>NH<sub>2</sub>.

The plot of log  $k''$  versus  $\sigma^*$  (where  $k''$  is the second order rate constant and  $\sigma^*$  the Taft's substituent constant) was linear (correlation coefficient 0.994) when ethyl amine was taken as standard indicating Taft's equation to be applicable and that polar effects are more prominent. This can be clearly seen from the large difference in the rate constants for the oxidation of ethyl amine ( $\sigma^*=0$ ) and methyl amine ( $\sigma^*H=0.48$ , Table 2). The  $\rho^*$  value, found from the slope of the linear plot was -5.41 (at 60°C) indicating the reaction to be substituent sensitive following an ionic mechanism. The high value for  $\rho^*$  has earlier been observed in H<sup>-</sup> ion transfer mechanism<sup>8</sup>. The negative  $\rho^*$  value indicates that the reaction is facilitated by high electron density at the  $\alpha$ -carbon atom, consistent with the reactivity order.

The study of the substituent effect also rules out attack at NH<sub>2</sub> group to bring about N-H bond rupture. If this were to be the case, then the plot of log  $k''$  versus  $\sigma^*$  should have been linear when methyl amine was taken as the standard instead of ethyl amine. Such linearity was not observed, supporting proposed mechanism.

Activation parameters have been calculated and listed in Table 3. The decrease in rate with decrease in dielectric constant of the medium (Table 1) and negative  $\Delta S^\ddagger$  values (Table 3) indicate that the solvent effect is predominant. The plot of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  was linear with a slope ( $\beta$ ) equal to 180 K, (correlation coefficient, 0.981) indicating the general applicability of isokinetic phenomenon. The isokinetic temperature ( $\beta$ ) is well below the experimental temperature range (328-372 K) used indica-

ting that the reaction is entropy-controlled. This is also evident from the fact that the fastest reaction has the highest  $\Delta S^\ddagger$  and vice versa.

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## Kinetics of Polymerization of Vinyl Stearate†

M. B. SABNE\* & N. RAJAGOPALAN  
 National Chemical Laboratory, Pune 411 008

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The kinetics of polymerization of vinyl stearate initiated by 2,2'-azobis (isobutyronitrile) have been studied in toluene solution at 75° and 80°C. The values of  $k_d$  for the initiator, and  $k_p/k_t^{1/2}$  for the monomer have been obtained from time-conversion studies under dead and polymerization conditions. The values of  $k_p/k_t^{1/2}$  for the monomer have also been determined from variation of initial rate of polymerization with initiator concentration at constant monomer concentration. Very low degree of polymerization (3 to 6) is obtained for this system, indicating very high chain transfer to monomer. Further, very high and varying monomer order, as in the case of vinyl acetate, is indicated in the present study.

VINYL stearate, a waxy solid, m.p. 35-36° (mol. wt 310.5) is known to polymerize by free radical initiation. A few reports pertaining to its radiation induced polymerization<sup>1,2</sup>, emulsion polymerization<sup>3</sup> and chain transfer constants<sup>4,5</sup> are available in literature. But no detailed investigation on the basic kinetic behaviour of this monomer has so far been made.

We have therefore studied the kinetics of polymerization of vinyl stearate in toluene solution initiated by 2,2'-azobis (isobutyronitrile) (AIBN) at 75° and 80° respectively.

Vinyl stearate (M/s Matheson Coleman) was purified<sup>5,6</sup> by distillation under N<sub>2</sub> atmosphere (166°-70°C at 1.6 mm) followed by treating its acetone solution with 6*N* aq. sodium hydroxide to precipitate the free fatty acid. The filtrate was chilled to crystallize the monomer which was repeatedly recrystallized from acetone till its melting

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