



Ru(III)-catalysed oxidation of some *N*-heterocycles by chloramine-T in hydrochloric acid medium: a kinetic and mechanistic study

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Abstract

The kinetics of the ruthenium(III) chloride (Ru(III))-catalysed oxidation of five *N*-heterocycles (S) viz. imidazole (IzIH), benzimidazole (BzIH), 2-hydroxybenzimidazole (2-HyBzIH), 2-aminobenzimidazole (2-AmBzIH) and 2-phenylbenzimidazole (2-PhBzIH) by sodium-*p*-toluenesulfonamide (chloramine-T; CAT) in the presence of HCl has been studied at 313 K. The oxidation reaction follows the identical kinetics for all the five *N*-heterocycles and obeys the rate law, $\text{rate} = k [\text{CAT}]_0 [\text{S}]_0^x [\text{H}^+]^y [\text{Ru(III)}]^z$, where x , y and z are less than unity. Addition of *p*-toluenesulfonamide (PTS) retards the reaction rate. Variation of ionic strength of the medium and the addition of halide ions show negligible effect on the rate of the reaction. The rate was found to increase in D₂O medium and showed positive dielectric effect. The reaction products are identified. The rates are measured at different temperatures for all substrates and the composite activation parameters have been computed from the Arrhenius plots. From enthalpy–entropy relationships and Exner correlations, the calculated isokinetic temperature (β) of 392 K is much higher than the experimental temperature (313 K), indicating that, the rate has been under enthalpy control. Relative reactivity of these substrates are in the order: 2-HyBzIH > 2-AmBzIH > BzIH > IzIH > 2-PhBzIH. This trend may be attributed to resonance and inductive effects. Further, the kinetics of Ru(III)-catalysed oxidation of these *N*-heterocycles have been compared with uncatalysed reactions (in the absence of Ru(III) catalyst) and found that the catalysed reactions are 16–20 times faster. The catalytic constant (K_C) was also calculated for each substrate at different temperatures. From the plots of $\log K_C$ versus $1/T$, values of activation parameters with respect to the catalyst have been evaluated. H₂O⁺Cl has been postulated as the reactive oxidizing species. The reaction mechanism and the derived rate law are consistent with the observed experimental results.

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1. Introduction

The *N*-heterocycles are of considerable importance as they are present in several living systems. Imidazole is an azopyrrole and its nucleus is found in a number of naturally occurring compounds such as histidine, histamine, pilocarpine, allantoin, etc. [1]. Benzimidazole occurs in Vitamin B₁₂ as its 5,6-dimethyl derivative. Benzimidazole and its derivatives have been extensively studied in various fields. Benzimidazole and a number of its derivatives perform a variety of bi-

ological functions [2,3]. A large number of benzimidazoles are known to possess trypanosomicidal and spirocheticidal action and are effective against diseases caused by protozoa [4]. A number of benzimidazoles have been reported to be used as local anaesthetics [4] and are also used in textile industries [4]. Benzimidazole and its derivatives form a variety of metal complexes [5,6] and also they serve as good inhibitors for the corrosion of large number of metals in different media [7,8].

Oxidation of benzimidazoles to imidazole carboxylic acids brought about by various oxidizing agents under different sets of conditions, have been reported in the literature [9]. But there seems to be no report on the oxidation ki-

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netics of benzimidazoles using any oxidant. Aromatic *N*-halosulfonamides are mild oxidants containing a strongly polarized *N*-halogen, with +1 oxidation state. They behave both as electrophiles and nucleophiles depending on the reaction conditions. Chloramine-T (CAT) is prominent chlorine derivative of this class of organic haloamines and is well known as an analytical reagent. Mechanistic aspects of many of its reactions have been reported [10,11].

In view of varied nature of *N*-halomines and extensive biological and industrial importance of benzimidazoles, it was felt important and interesting to investigate the oxidative behaviour of CAT towards imidazole and benzimidazoles. The reactions of imidazole and benzimidazoles with CAT in the presence of HCl medium without a catalyst were found to be sluggish, but the reactions were found to be facile in the presence of Ru(III) chloride catalyst. Therefore, in the present communication, we report the results of the investigation on the mechanistic and kinetic aspects of oxidation of imidazole, benzimidazole, 2-hydroxybenzimidazole, 2-aminobenzimidazole and 2-phenylbenzimidazole by CAT in the presence of HCl and Ru(III) catalyst at 313 K. The objectives of the present investigation are to: (i) elucidate a suitable mechanism, (ii) put forward an appropriate rate law, (iii) ascertain the reactive species, (iv) assess the relative reactivities of the substrates, (v) establish the isokinetic relationships using thermodynamic parameters evaluated, (vi) find the catalytic efficiency and (vii) compare the reactivity with uncatalysed oxidation.

2. Results and discussion

The kinetics of oxidation of imidazole (IzIH), benzimidazole (BzIH), 2-hydroxybenzimidazole (2-HyBzIH), 2-aminobenzimidazole (2-AmBzIH) and 2-phenylbenzimidazole (2-PhBzIH) by CAT have been investigated at several initial concentrations of the reactants in the presence of HCl and Ru(III) chloride catalyst at 313 K.

2.1. Effect of varying reactant concentrations on the rate

The reaction carried out in the presence of Ru(III) catalyst and HCl, under pseudo first-order conditions of $[\text{substrate}]_0 \gg [\text{CAT}]_0$ gave linear plots of $\log[\text{CAT}]$ versus time ($r=0.9960$). The linearity of these plots, together with the constancy of the slopes obtained at various $[\text{CAT}]_0$, indicate a first-order dependence of the reaction rate on $[\text{CAT}]_0$. The pseudo first-order rate constants (k') obtained are listed in Table 1. Under the similar experimental conditions, an increase in $[\text{substrate}]_0$ increased the k' values (Table 1). Plots of $\log k'$ versus $\log[\text{substrate}]_0$ were linear ($r>0.9970$) with fractional slopes (0.35–0.59), showing a fractional-order dependence of rate on $[\text{substrate}]_0$. Further, plots of k' versus $[\text{substrate}]_0$ were linear ($r>0.9902$) having a Y -intercept, confirming the fractional-order dependence on $[\text{substrate}]_0$.

2.2. Effect of varying HCl and Ru(III) concentrations on the rate

The rate increased with increase in $[\text{HCl}]$ (Table 2) and plots of $\log k'$ versus $\log[\text{HCl}]$ were linear ($r>0.9956$) with fractional slopes (0.26–0.73), showing a fractional-order dependence of the rate on $[\text{HCl}]$. The reaction rate increased with increase in $[\text{Ru(III)}]$ (Table 2). Plots of $\log k'$ versus $\log[\text{Ru(III)}]$ were linear ($r>0.9972$) with fractional slopes (0.67–0.72), confirming fractional-order dependence on $[\text{Ru(III)}]$.

2.3. Effect of varying H^+ and halide ion concentrations on the rate

At constant $[\text{H}^+]=0.01 \text{ mol dm}^{-3}$ maintained with HCl, the addition of NaCl (2.0×10^{-2} to $8.0 \times 10^{-2} \text{ mol dm}^{-3}$) did not affect the rate of the reaction. Hence the dependence of rate on $[\text{HCl}]$ confirms the effect of $[\text{H}^+]$ only. Similarly, addition of Br^- ions as of NaBr (1.0×10^{-3} to $5.0 \times 10^{-3} \text{ mol dm}^{-3}$) had no effect on the rate. These results indicate that the halide ions play no role in the reaction.

Table 1
Effect of varying reactant concentrations on the reaction rate at 313 K

$10^4[\text{CAT}]_0 \text{ (mol dm}^{-3}\text{)}$	$10^3[\text{S}]_0 \text{ (mol dm}^{-3}\text{)}$	$10^4k' \text{ (s}^{-1}\text{)}$				
		IzIH	BzIH	2-HyBzIH	2-AmBzIH	2-PhBzIH
1.0	2.0	5.14	6.04	11.5	8.62	4.79
2.0	2.0	5.04	6.14	11.9	8.60	4.82
4.0	2.0	5.16	6.10	11.9	8.61	4.83
5.0	2.0	5.20	6.06	11.5	8.63	4.80
6.0	2.0	5.15	6.11	11.9	8.62	4.84
2.0	1.0	4.02	4.27	9.33	6.88	3.60
2.0	1.5	4.60	5.20	10.6	7.60	4.30
2.0	2.0	5.04	6.14	11.9	8.60	4.82
2.0	3.0	5.90	7.88	13.3	10.2	5.95
2.0	4.0	6.60	9.32	14.8	11.0	7.06

$[\text{HCl}]=1.0 \times 10^{-2} \text{ mol dm}^{-3}$; $[\text{RuCl}_3]=1.0 \times 10^{-4} \text{ mol dm}^{-3}$.

Table 2
Effect of varying HCl and Ru(III) concentrations on the reaction rate at 313 K

$10^2[\text{HCl}]$ (mol dm ⁻³)	$10^4[\text{RuCl}_3]$ (mol dm ⁻³)	$10^4k'$ (s ⁻¹)				
		IzIH	BzIH	2-HyBzIH	2-AmBzIH	2-PhBzIH
0.5	1.0	3.57	4.37	8.06	6.40	3.70
1.0	1.0	5.04	6.14	11.9	8.60	4.82
2.0	1.0	6.88	8.45	18.0	12.3	6.90
3.0	1.0	7.45	10.1	21.0	14.8	8.00
4.0	1.0	9.40	11.5	24.3	17.4	9.10
1.0	0.5	3.25	3.85	7.58	5.65	2.91
1.0	0.8	4.50	5.20	10.2	7.60	4.00
1.0	1.0	5.04	6.14	11.9	8.60	4.82
1.0	1.5	7.10	7.95	15.8	11.5	6.35
1.0	2.0	8.75	10.0	19.1	14.4	8.05

$[\text{CAT}]_0 = 2.0 \times 10^{-4}$ mol dm⁻³; $[\text{S}]_0 = 2.0 \times 10^{-3}$ mol dm⁻³.

2.4. Effect of varying concentration of *p*-toluenesulfonamide (PTS) on the rate

Addition of PTS to the reaction mixture retards the rate. Plots of $\log k'$ versus $\log[\text{PTS}]$ were linear ($r > 0.9898$) with negative fractional slopes (0.28–0.40; values are not reported), indicating the involvement of PTS in a pre-equilibrium step prior to the rate determining step (r.d.s.).

2.5. Effect of varying ionic strength of the medium on the rate

The effect of ionic strength of the medium on the rate was carried from 0.1 to 0.5 mol dm⁻³ using NaClO₄ solution with other constant experimental conditions. The ionic strength showed negligible effect on the reaction rate indicating involvement of a non-ionic species in the rate determining step. Subsequently the ionic strength of the reaction mixture was not fixed.

2.6. Effect of varying dielectric constant of the medium on the rate

The dielectric constant (D) of the medium was varied using methanol (0–30%, v/v) in the reaction mixture. The rate increases with increase in methanol content (Table 3). Plots of $\log k'$ versus $1/D$ were linear ($r > 0.9976$) with positive slopes. Blank experiments run with methanol indicated negli-

Table 3
Effect of varying dielectric constant of the medium on the reaction rate at 313 K

MeOH (% , v/v)	$10^4k'$ (s ⁻¹)				
	IzIH	BzIH	2-HyBzIH	2-AmBzIH	2-PhBzIH
0	5.04	6.14	11.9	8.60	4.82
5	11.9	14.1	15.3	15.5	10.4
10	15.9	17.5	20.4	20.2	14.2
30	28.1	32.6	36.2	33.3	26.6

$[\text{CAT}]_0 = 2.0 \times 10^{-4}$ mol dm⁻³; $[\text{S}]_0 = 2.0 \times 10^{-3}$ mol dm⁻³;
 $[\text{HCl}] = 1.0 \times 10^{-2}$ mol dm⁻³; $[\text{RuCl}_3] = 1.0 \times 10^{-4}$ mol dm⁻³.

gible oxidation under the experimental conditions employed. Values of dielectric constant of methanol–water mixture reported in the literature [12] were employed.

2.7. Effect of varying temperature on the rate

The reaction was studied at different temperatures (303–323 K), keeping other experimental conditions constant. From the linear Arrhenius plots of $\log k'$ versus $1/T$ ($r > 0.9965$), values of activation parameters (E_a , ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger) for the composite reaction were evaluated. These data are given in Table 4.

2.8. Effect of solvent isotope on the rate

Studies of the reaction rate in D₂O medium for imidazole, benzimidazole and 2-hydroxybenzimidazole revealed that while $k'(\text{H}_2\text{O}) = 5.04 \times 10^{-4}$, 6.14×10^{-4} , and 11.9×10^{-4} s⁻¹ and $k'(\text{D}_2\text{O}) = 5.90 \times 10^{-4}$, 7.75×10^{-4} , and 14.6×10^{-4} s⁻¹, respectively. The solvent isotope effect $k'(\text{H}_2\text{O})/k'(\text{D}_2\text{O}) = 0.85$, 0.79 and 0.82 for these three substrates.

2.9. Test for free radicals

The addition of the reaction mixture to an aqueous acrylamide monomer solution did not initiate polymerization indicating the absence of formation of free radical species in situ in the reaction sequence. The controlled experiments were also performed under the same reaction conditions but without CAT.

Chloramine-T acts as a mild oxidant in both acidic and alkaline media. In general, CAT undergoes a two-electron change in its reactions forming the reduction products, PTS (*p*-CH₃C₆H₄SO₂NH₂) and sodium chloride. The oxidation potential of CAT–PTS redox couple varies [13] with pH of the medium (1.139 V at pH 0.65, 0.778 V at pH 7.0 and 0.614 V at pH 9.7). Aqueous solution of CAT behaves as a strong electrolyte and depending on the pH, CAT furnishes different types of reactive species [13–15]. The possible ox-

Table 4

Temperature dependence and values of composite activation parameters for the oxidation of *N*-heterocycles by CAT in presence and absence of Ru(III) catalyst

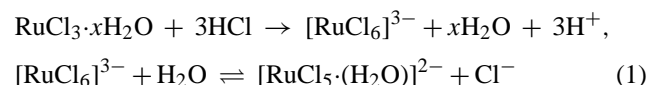
Temperature (K)	$10^4 k'$ (s ⁻¹)				
	IzIH	BzIH	2-HyBzIH	2-AmBzIH	2-PhBzIH
303	2.53 ^a (0.10) ^b	3.45 (0.13)	6.35 (0.23)	5.00 (0.17)	2.50 (0.07)
308	3.98 (0.18)	4.73 (0.21)	9.12 (0.45)	6.75 (0.32)	3.45 (0.13)
313	5.04 (0.28)	6.14 (0.37)	11.9 (0.68)	8.60 (0.49)	4.82 (0.24)
318	7.58 (0.57)	8.91 (0.64)	16.2 (1.13)	11.6 (0.81)	6.92 (0.41)
323	10.1 (0.84)	12.0 (1.00)	22.1 (1.46)	15.4 (1.21)	9.50 (0.75)
E_a (kJ mol ⁻¹)	54.4 (100)	53.6 (95.8)	45.2 (77.2)	48.3 (88.3)	58.7 (105)
ΔH^\ddagger (kJ mol ⁻¹)	51.8 ± 0.2 (97.9 ± 0.1)	50.9 ± 0.1 (93.2 ± 0.2)	42.6 ± 0.2 (74.5 ± 0.1)	45.7 ± 0.1 (85.7 ± 0.3)	56.1 ± 0.2 (102 ± 0.2)
ΔG^\ddagger (kJ mol ⁻¹)	96.5 ± 0.4 (104 ± 0.6)	95.9 ± 0.7 (103 ± 0.4)	94.3 ± 0.5 (102 ± 0.5)	95.1 ± 0.9 (103 ± 0.5)	96.7 ± 0.8 (105 ± 0.5)
ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	-142 ± 0.2 (-19.6 ± 0.5)	-144 ± 0.4 (-32.7 ± 0.6)	-165 ± 0.8 (-87.2 ± 0.9)	-158 ± 0.9 (-54.2 ± 0.6)	-130 ± 0.4 (-8.36 ± 0.9)

Values in parentheses refer to the reaction in absence of Ru(III) catalyst.

^a [CAT]₀ = 2.0 × 10⁻⁴ mol dm⁻³; [S]₀ = 2.0 × 10⁻³ mol dm⁻³; [HCl] = 1.0 × 10⁻² mol dm⁻³; [RuCl₃] = 1.0 × 10⁻⁴ mol dm⁻³.^b Experimental condition is same as above without Ru(III) catalyst.

idizing species in acidified CAT solutions are dichloramine-T (TsNCl₂), the conjugate free acid (TsNHCl), HOCl and H₂O⁺Cl. If TsNCl₂ were to be the reactive species, then the rate law predicts the second-order dependence on [CAT]₀, which is not in agreement with experimental observations, since a first-order with respect to [CAT]₀ was noted. If HOCl act as a reactive oxidant species, a first-order retardation of rate on added PTS (TsNH₂) was expected. However, there was no such effect is seen, since a negative fractional order with respect to PTS was observed. The rate increased with increase in [H⁺] but gets retarded by the added PTS.

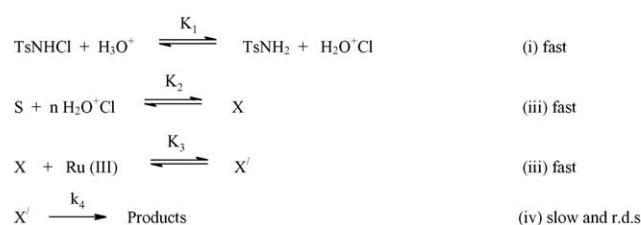
Although Cady and Connick [16], and Connick and Fine [17] have shown from absorption spectral studies in aqueous media that octahedral complexes such as [RuCl₅·(H₂O)]²⁻, [RuCl₄·(H₂O)₂]⁻, [RuCl₃·(H₂O)₃], [RuCl₂·(H₂O)₄]⁺ and [RuCl·(H₂O)₅]²⁺ do not exist for RuCl₃, others [18–20] have shown that in acid solutions the following equilibria exists for Ru(III):



Singh et al. [21,22] used the above equilibrium in the Ru(III) chloride catalysed oxidation of primary alcohols by chloramine-T and of glycols by *N*-bromoacetamide in acid medium. In the present study, however, the absence of the effect of chloride ion on the rate indicates that equilibrium (1) has no role in the reaction, hence, [RuCl₅·(H₂O)]²⁻ complex ion, has been assumed to be the reactive catalysing species. Similar results were observed in Ru(III)-catalysed oxidation of chloroacetic acids [23], ethanols [24] and aliphatic primary amines [25] by bromamine-T.

Based on the preceding discussion, a detailed mechanistic interpretation (Scheme 1) for the Ru(III) catalysed imidazole and benzimidazoles - CAT reaction in acid medium has been proposed to substantiate the observed kinetics:

Here *n* = 3 for imidazole, 2 for benzimidazole and 1 for 2-hydroxybenzimidazole, 2-aminobenzimidazole and 2-phenylbenzimidazole. In Scheme 1, S, X and X' represents the substrate and complex intermediate species whose struc-



Scheme 1.

tures are shown in Schemes 2–4, where a detailed mechanistic interpretation of the Ru(III) catalysed selected *N*-heterocycles–CAT reaction in acid medium is illustrated.

Assuming a total effective concentration of CAT, [CAT]_t = [TsNHCl] + [H₂O⁺Cl] + [X] + [X'], the following rate law can be derived:

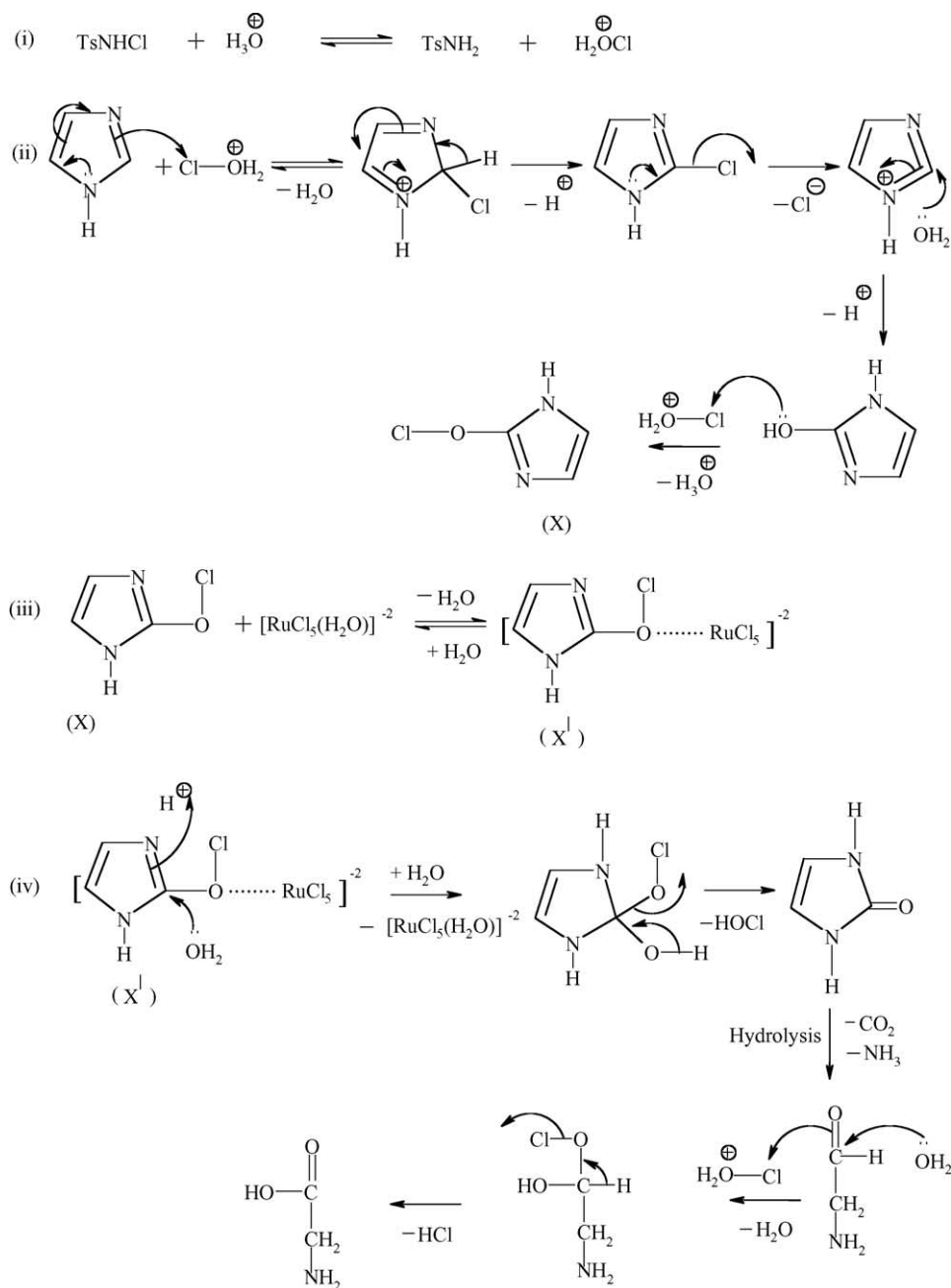
$$\begin{aligned} \text{rate} &= -\frac{d[\text{CAT}]}{dt} \\ &= \frac{K_1 K_2 K_3 k_4 [\text{CAT}]_t [\text{S}] [\text{H}_3\text{O}^+] [\text{Ru(III)}]}{[\text{TsNH}_2] + K_1 [\text{H}_3\text{O}^+] + K_1 K_2 [\text{S}] [\text{H}_3\text{O}^+] \{1 + K_3 [\text{Ru(III)}]\}} \quad (2) \end{aligned}$$

Since rate = *k'*[CAT]_t, Eq. (2) can be transformed into Eqs. (3)–(5):

$$k' = \frac{K_1 K_2 K_3 k_4 [\text{H}_3\text{O}^+] [\text{Ru(III)}]}{[\text{TsNH}_2] + K_1 [\text{H}_3\text{O}^+] + K_1 K_2 [\text{S}] [\text{H}_3\text{O}^+] \{1 + K_3 [\text{Ru(III)}]\}} \quad (3)$$

$$\begin{aligned} \frac{1}{k'} &= \frac{[\text{TsNH}_2]}{K_1 K_2 K_3 k_4 [\text{H}_3\text{O}^+] [\text{Ru(III)}]} + \frac{1}{K_2 K_3 k_4 [\text{S}] [\text{Ru(III)}]} \\ &+ \frac{1}{K_3 k_4 [\text{Ru(III)}]} + \frac{1}{k_4} \quad (4) \end{aligned}$$

$$\frac{1}{k'} = \frac{1}{K_3 k_4 [\text{Ru(III)}]} \left\{ \frac{[\text{TsNH}_2]}{K_1 K_2 [\text{S}] [\text{H}_3\text{O}^+]} + \frac{1}{K_2 [\text{S}]} + 1 \right\} + \frac{1}{k_4} \quad (5)$$



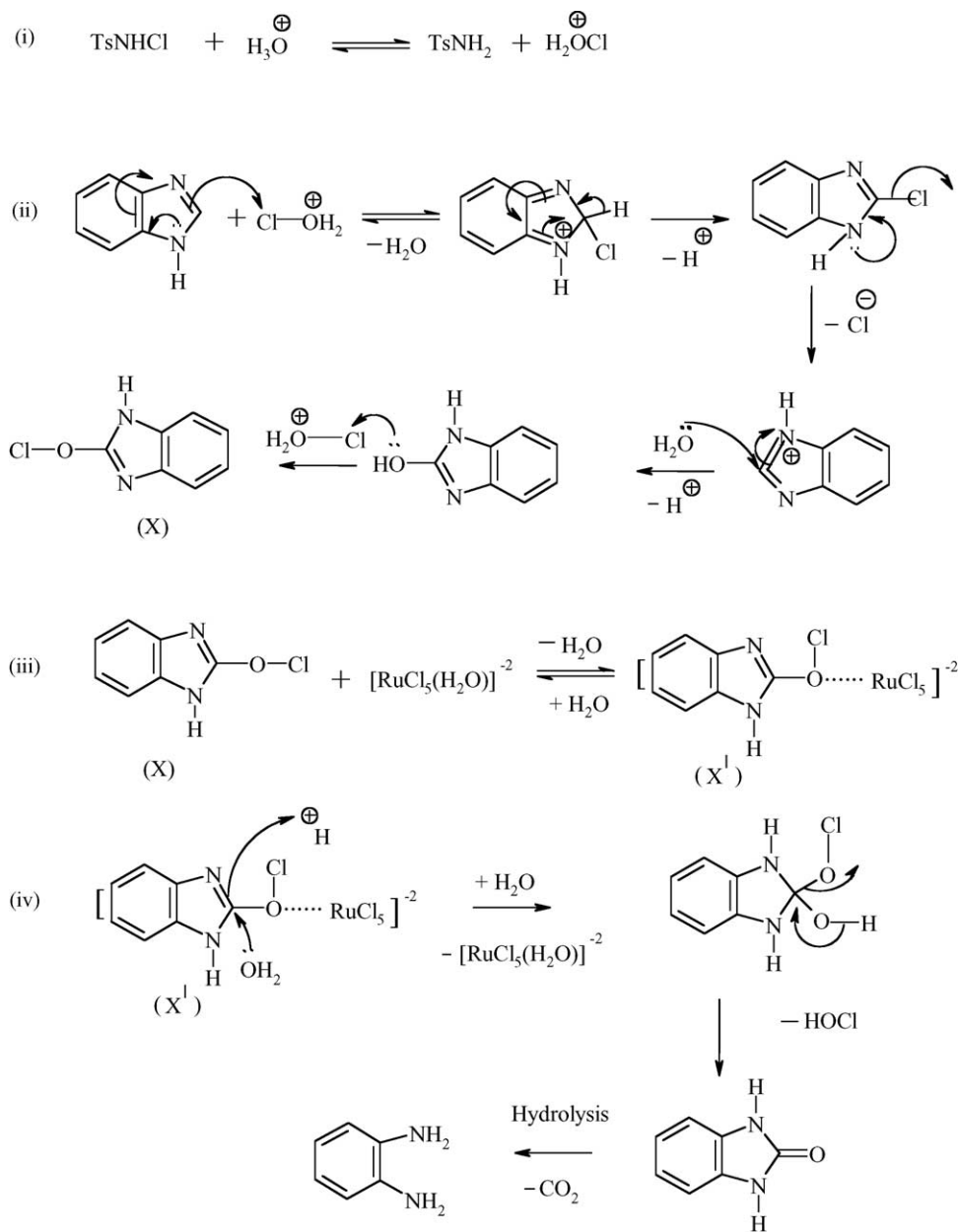
Scheme 2. Oxidation of imidazole.

Based on Eq. (5), plots of $1/k'$ versus $1/[\text{Ru(III)}]$ at constant $[\text{S}]$, $[\text{H}^+]$ and temperature, were found to be linear ($r > 0.9916$) for each substrate. Decomposition constant (k_4) was calculated for each substrate from the intercepts of the above plots for the standard run with $[\text{CAT}]_0 = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$; $[\text{S}]_0 = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$; $[\text{HCl}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ at 313 K. Values of k_4 found were $10^3 k_4 \text{ s}^{-1}$: 2.00 (IzIH), 2.50 (BzIH), 4.00 (2-HyBzIH), 3.33 (2-AmBzIH) and 1.25 (2-PhBzIH).

Rate law (2) is in agreement with the observed kinetic data. The proposed scheme and the derived rate law are also supported by the experimental observations discussed below.

2.10. Effect of solvent isotope

The solvent isotope effect observed corroborates the proposed mechanism and the derived rate expression. For a reaction involving a fast equilibrium H^+ or OH^- ion transfer, the rate increases in D_2O since D_3O^+ and OD^- which are stronger acid and stronger base ($\sim 2\text{--}3$ times greater), respectively, than H_3O^+ and OH^- ions [26,27]. The increase of reaction rate with D_2O observed in the present studies and the solvent isotope effect which is $k'(\text{H}_2\text{O})/k'(\text{D}_2\text{O}) < 1$ conform to the above theory. The small magnitude of the effect can be attributed to the fractional order dependence on $[\text{H}^+]$.



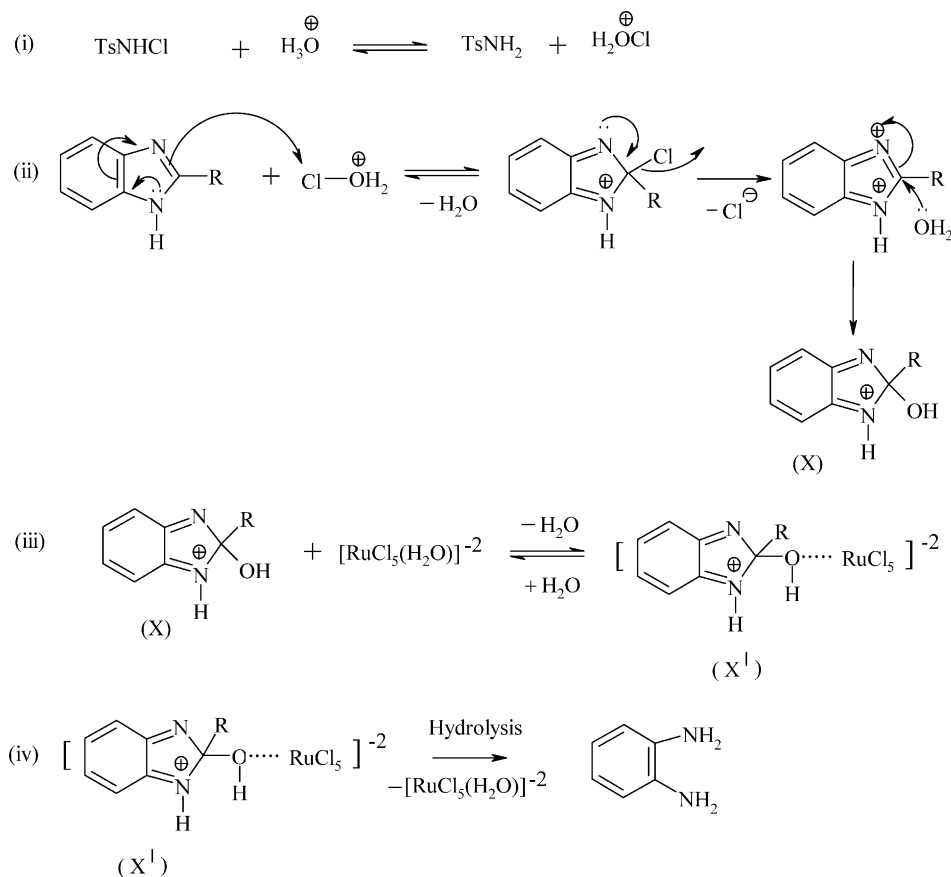
Scheme 3. Oxidation of benzimidazole.

2.11. Effect of solvent composition

The effect of solvent on the reaction kinetics has been described in detail by Laidler and Eyrings [28] and Emis [29]. For limiting case of zero angle of approach between two dipoles or an ion-dipole system, Emis [29] has shown that a plot of $\log k'$ versus $1/D$ gives a straight line, with a positive slope for a reaction involving a positive ion and a dipole and a negative slope for a negative ion-dipole or dipole-dipole interactions. In the present investigations, a plot of $\log k'$ versus $1/D$ was linear with a positive slope. This observation indicates the ion-dipole nature of the rate-determining step in the reaction sequence and also points to extending of charge in the transition state.

2.12. Activation parameters in presence of Ru(III)

It is seen from the Table 4 that the rate of oxidation of *N*-heterocycles by CAT in presence of HCl and Ru(III) catalyst increased in the order: 2-HyBzIH > 2-AmBzIH > BzIH > IzIH > 2-PhBzIH. The reactivity of benzimidazole is faster compared to imidazole mainly because of resonance structure. In benzimidazole, more number of resonance structures are possible due to phenyl ring, whereas in case of imidazole possible number of resonance structures are less due to the absence of the phenyl ring. Further, 2-hydroxybenzimidazole is found to react fast in the present study because of the presence of electron donating -OH group. The higher reactivity of 2-hydroxybenzimidazole in



Here R = OH for 2-HyBzIH, NH₂ for 2-AmBzIH and Ph for 2-PhBzIH. The other oxidation products are: CO₂ in case of 2-HyBzIH, CO₂ and NH₃ in case of 2-AmBzIH and PhCOOH in case of 2-PhBzIH.

Scheme 4. Oxidation of 2-hydroxybenzimidazole, 2-aminobenzimidazole and 2-phenylbenzimidazole.

comparison with 2-aminobenzimidazole can be attributed due to the differences in the electron donating effect of –OH and –NH₂ groups. Furthermore, 2-phenylbenzimidazole is least reactive in the present series because electron density on nitrogen decreases due to the negative inductive effect of the phenyl group present in position 2.

The activation energy value is highest for the slowest reaction and vice versa as expected (Table 5) indicating that the reaction is enthalpy controlled. The isokinetic temperature was calculated by plotting ΔH^{\ddagger} versus ΔS^{\ddagger} ($r = 0.9995$) and also through the Exner criterion [30] by plotting $\log k'_{(313\text{K})}$ versus $\log k'_{(303\text{K})}$ ($r = 0.9919$) and were found to be 392 K. The calculated β value from both the plots are much higher than the temperature range (303–323 K) studied in the present work shows that the reaction is enthalpy controlled. In the literature it is substantiated that for a large number of reactions in which β is higher than the experimental temperature [31–33], the reactions are enthalpy-controlled. The proposed mechanism is also supported by the moderate values of energy of activation and other activation parameters. The high positive values of ΔG^{\ddagger} and ΔH^{\ddagger} indicate that the transition state is highly solvated. The large negative values of ΔS^{\ddagger} reflect a more ordered, rigid transition state for each substrate.

2.13. Activation parameters in absence of Ru(III)

It was thought necessary to compare the reactivity of five *N*-heterocycles by oxidizing them with CAT in the absence of Ru(III) catalyst under identical experimental conditions. The reactions were studied at different temperatures (303–323 K)

Table 5
Values of catalytic constant (K_C) at different temperatures and activation parameters calculated using K_C values

Temperature (K)	10 K_C					
	IzIH	BzIH	2-HyBzIH	2-AmBzIH	2-PhBzIH	
303	1.84	2.10	4.00	2.31	1.15	
308	2.50	2.86	4.98	3.05	1.60	
313	3.57	3.65	6.45	3.90	2.20	
318	5.00	5.30	8.66	5.76	3.11	
323	6.75	7.00	11.8	7.20	4.20	
E_a (kJ mol ⁻¹)		47.2	42.7	34.3	39.8	50.4
ΔH^{\ddagger} (kJ mol ⁻¹)		45.1	40.1	31.7	35.2	47.8
ΔG^{\ddagger} (kJ mol ⁻¹)		79.6	79.5	78.3	79.3	79.9
ΔS^{\ddagger} (J K ⁻¹ mol ⁻¹)		-110	-126	-148	-135	-103

[CAT]₀ = 2.0 × 10⁻⁴ mol dm⁻³; [S]₀ = 2.0 × 10⁻³ mol dm⁻³;
[HCl] = 1.0 × 10⁻² mol dm⁻³.

and from the plot of $\log k'$ versus $1/T$ ($r > 0.9920$), activation parameters for the uncatalysed reactions were calculated. The rate of oxidation of *N*-heterocycles in the absence of Ru(III) catalyst was found to be in the order: 2-HyBzIH > 2-AmBzIH > BzIH > IzIH > 2-PhBzIH. A similar trend results in the presence of Ru(III) catalyst also. However, the Ru(III) catalysed reactions were found to be 16–20 times faster than the uncatalysed reactions. This was also confirmed by the calculated activation parameters (Table 4). Thus, the observed rates of oxidation obtained in the presence of Ru(III) justify the use of a catalyst for a facile oxidation of the chosen substrates by CAT. Further the results also suggest that Ru(III) is an efficient catalyst in effecting the oxidation of *N*-heterocycles by CAT in acid medium.

The activation parameters evaluated for the catalysed and uncatalysed reactions explains the catalytic effect on the reaction. The catalyst Ru(III) forms the complex (X') with substrate–oxidant complex (X), which enhances the reducing property of the substrate than that without Ru(III). Further, the catalyst Ru(III) modifies the reaction path by lowering the energy of activation.

2.14. Catalytic activity

It has been pointed out by Moelwyn-Hughes [34] that in presence of the catalyst, the uncatalysed and catalysed reactions proceed simultaneously, so that

$$k_1 = k_0 + K_C[\text{catalyst}]^x \quad (6)$$

Here k_1 is the observed pseudo first-order rate constant in the presence of Ru(III) catalyst, k_0 the pseudo first-order rate constant for the uncatalysed reaction, K_C the catalytic constant and x the order of the reaction with respect to [Ru(III)]. In the present investigations, x values for the standard run were found to be: 0.72 (IzIH), 0.70 (BzIH), 0.69 (2-HyBzIH), 0.67 (2-AmBzIH) and 0.67 (2-PhBzIH). Then the value of K_C is calculated using the equation

$$K_C = \frac{k_1 - k_0}{[\text{Ru(III)}]^x} \quad (7)$$

The values of K_C were evaluated for each substrate at different temperatures and found to vary at different temperatures. Further, plots of $\log K_C$ versus $1/T$ were linear ($r > 0.9922$) and the values of energy of activation and other activation parameters with reference to catalyst were computed. These results are summarized in Table 5.

3. Conclusion

Oxidation of imidazole (IzIH), benzimidazole (BzIH), 2-hydroxybenzimidazole (2-HyBzIH), 2-aminobenzimidazole (2-AmBzIH) and 2-phenylbenzimidazole (PhBzIH) by chloramine-T in HCl medium is very sluggish but the reactions are facile in the presence of Ru(III) catalyst. The rate

of oxidation of *N*-heterocycles was found to be in the order: 2-HyBzIH > 2-AmBzIH > BzIH > IzIH > 2-PhBzIH. The order has been explained on the basis of resonance and inductive effects. Kinetic behaviour of all the substrates is similar. Oxidation products were identified. Activation parameters were evaluated for both catalysed and uncatalysed reactions. Catalytic constants and the activation parameters with reference to catalyst were also computed. Ru(III)-catalysed reactions were found to proceed 16–20 times faster than the uncatalysed reactions. In conclusion, it can be said that Ru(III) is an efficient catalyst in the oxidation of the selected *N*-heterocycles by CAT in acid medium.

4. Experimental

4.1. Materials

Chloramine-T (Merck) was purified by the method of Morris et al. [35]. An aqueous solution of CAT was prepared, standardized iodometrically and stored in amber-colored, stoppered bottles until further use. The concentration of stock solutions was periodically determined. Imidazole and benzimidazoles (SD Fine Chem. Ltd., India), 2-aminobenzimidazole and 2-phenylbenzimidazole (Lancaster, UK) 2-hydroxybenzimidazole (Fluka, Switzerland) were of acceptable grades of purity and were used as received. Aqueous solutions of the compounds are employed. A solution of RuCl_3 (Merck) in 0.5 mol dm^{-3} HCl was used as the catalyst. Allowance was made for the amount of HCl present in catalyst solution, while preparing solution for kinetic runs. Solvent isotope studies were made in D_2O (99.4%) supplied by Bhabha Atomic Research Center, Mumbai, India. Reagent grade chemicals and doubly distilled water were used throughout.

4.2. Kinetic measurements

The reactions were carried out under pseudo first-order conditions by taking a known excess of $[\text{substrate}]_0$ over $[\text{oxidant}]_0$ at 313 K. The reaction was carried out in stoppered Pyrex boiling tubes whose outer surfaces were coated black to eliminate photochemical effects. For each run, requisite amounts of solutions of substrate, HCl, RuCl_3 and water (to keep the total volume constant for all runs) were taken in the tube and thermostated at 313 K until thermal equilibrium was attained. A measured amount of CAT solution, which was also thermostated at the same temperature, was rapidly added with stirring to the mixture in the tube. The course of the reaction was monitored by the iodometric determination of unreacted CAT in 5 ml of aliquots of the reaction mixture withdrawn at different intervals of time. The course of the reaction was studied for at least two half-lives. The pseudo first-order rate constants (k') calculated from the linear plots of $\log[\text{CAT}]$ versus time were reproducible within $\pm 5\%$. Re-

gression analysis of experimental data to obtain regression coefficient, r , was performed using a fx-100W scientific calculator.

4.3. Stoichiometry

Reaction mixtures containing varying ratios of CAT to *N*-heterocycles in the presence of HCl and RuCl₃ were equilibrated at 313 K for 48 h. Estimation of the unreacted CAT showed that one mole of the substrate utilized three moles of the oxidant in the case of imidazole, two moles in the case of benzimidazole and one mole in the case of 2-hydroxybenzimidazole, 2-aminobenzimidazole and 2-phenylbenzimidazole. The observed stoichiometry can be represented by Eqs. (8)–(12):

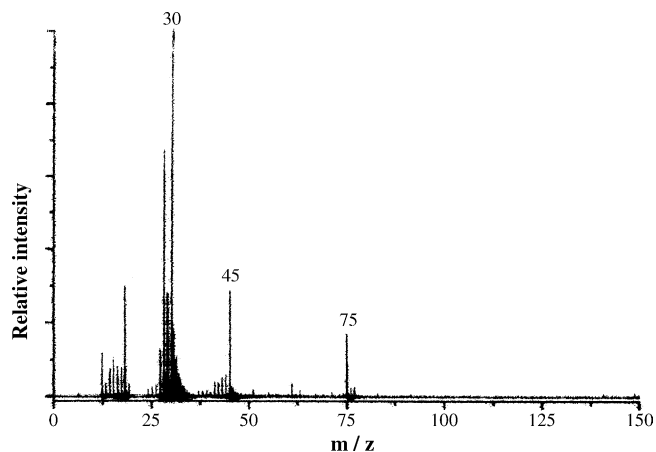
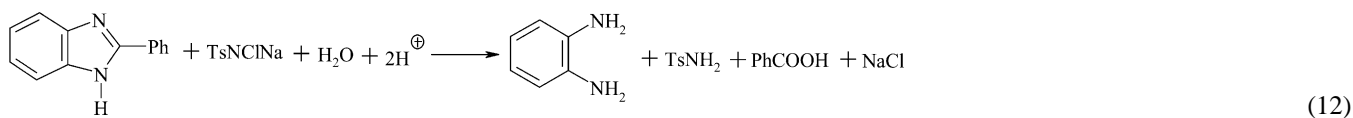
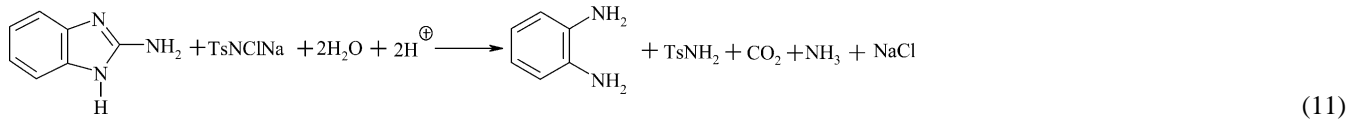
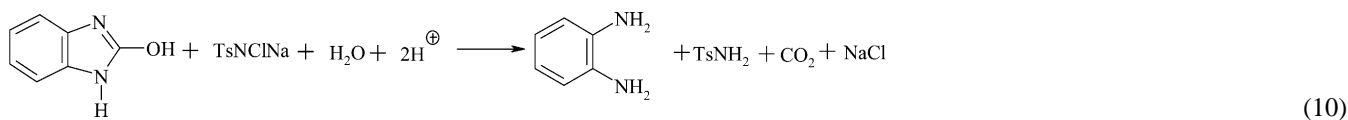
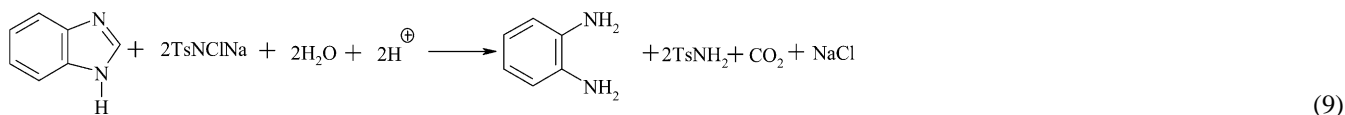
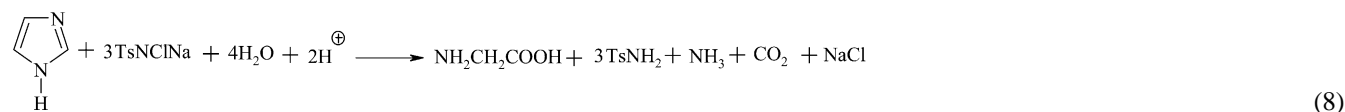


Fig. 3. GC-MS of glycine.

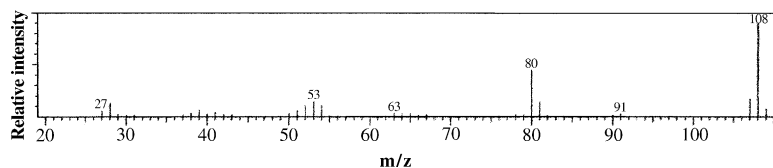


Fig. 1. GC-MS of *o*-phenylenediamine.

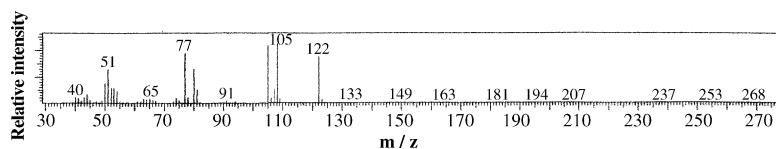


Fig. 2. GC-MS of benzoic acid.

4.4. Product analysis

The reaction products were neutralized with NaOH and extracted with ether. The organic products were subjected to spot tests and chromatographic analysis (TLC technique), which revealed that the formation of oxidation product was *o*-phenylenediamine [36] in the case of benzimidazole, 2-hydroxybenzimidazole and 2-aminobenzimidazole, whereas in the case of 2-phenylbenzimidazole the oxidation products were *o*-phenylenediamine and benzoic acid. Further, all these oxidation products were confirmed by their melting points; *o*-phenylenediamine 102 °C (Lit m.p. 103–104 °C) and benzoic acid 124 °C (Lit m.p. 122.4 °C) and comparing them with the authentic samples by TLC analysis. Glycine was the oxidation product in the case of imidazole, which was detected by spot tests [37]. Further, all these main oxidation products were confirmed by GC–MS (Figs. 1–3). The reduction product of CAT, TsNH₂, was identified [24] by TLC. It was further confirmed by its melting point of 138 °C (Lit m.p. 137–140 °C). The liberated CO₂ and NH₃ were identified by the conventional limewater and Nessler's reagent tests, respectively.

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