

Scheme 1

line medium. The observed $p\text{H}$ -rate profile indicates that the contribution to the rate through the dianionic tetrahedral addition intermediate is almost negligible probably due to the presence of ionized phenolic group. The steady state treatment to the reactive tetrahedral addition intermediate (D) leads to the kinetic Eqn (2).

$$K_{\text{obs}} = \frac{k_1 k_2 \frac{K_{a_1}}{K_w} [\text{OH}^-]^2}{(k_{-1} + k_2) \left(1 + \frac{K_{a_1}}{K_w} [\text{OH}^-] + \frac{K_{a_1}}{K_w} \cdot \frac{K_{a_2}}{K_w} [\text{OH}^-]^2 \right)} \quad \dots(2)$$

The Eqn (2) is further reduced to the Eqn (3) by applying the condition that

$$1 < \left(\frac{K_{a_1}}{K_w} [\text{OH}^-] + \frac{K_{a_1}}{K_w} \cdot \frac{K_{a_2}}{K_w} [\text{OH}^-]^2 \right)$$

which is satisfactorily acceptable as K_{a_1} is of the order $\sim 10^{-8}$.

$$K_{\text{obs}} = \frac{k_1 k_2 [\text{OH}^-]}{(k_{-1} + k_2) \left(1 + \frac{K_{a_2}}{K_w} [\text{OH}^-] \right)} \quad \dots(3)$$

Eqn (3) is similar to the best fitted empirical Eqn (1) with

$$B_1 = \frac{(k_{-1} + k_2)}{k_1 k_2} \cdot \frac{K_{a_2}}{K_w} \quad \text{and} \quad B_2 = \frac{(k_{-1} + k_2)}{k_1 k_2}$$

At relatively higher $[\text{OH}^-]$ the condition that $1 < \frac{K_{a_2}}{K_w} [\text{OH}^-]$ is found to be kinetically more pronounced and hence Eqn (3) is further reduced to Eqn (4),

$$K_{\text{obs}} = \frac{k_1 k_2}{(k_{-1} + k_2) K_{a_2} / K_w} \quad \dots(4)$$

which shows that the rate is independent of $[\text{OH}^-]$.

The authors thank Prof. W. Rahman for providing facilities, and the CSIR, New Delhi, for financial assistance to two of them (R.A. and M.N.K.).

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Kinetics of Oxidation of Cinnamyl Alcohol with Chloramine-T in Hydrochloric Acid Medium

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Received 15 July 1975; accepted 6 March 1976

The kinetics of oxidation of cinnamyl alcohol by chloramine-T in the presence of hydrochloric acid (0.1-0.3M) has been studied at 0°. The reaction shows first order dependence on [chloramine-T], second order in $[\text{H}^+]$ and is independent of [substrate]. The energy and entropy of activation of the reaction have been found to be 57.2 KJ mole⁻¹ and -75.01 JK⁻¹ respectively. The Arrhenius factor is $1.203 \times 10^9 \text{ sec}^{-1}$. Ionic strength and presence of *p*-toluenesulphonamide have very little influence on the rate of reaction. The proposed mechanism assumes a stepwise addition of two protons to release the precursor chlorinium ion, which on hydrolysis yields H_2OCl^+ . The latter attacks the substrate in a fast step to form the reaction products, cinnamic aldehyde and *p*-toluenesulphonamide.

IT was earlier¹ noticed that cinnamyl alcohol in 50% aq. ethanol (v/v) underwent ready oxidation by chloramine-T (CAT) in the presence of HCl (0.1 to 0.3M). The results of kinetic studies of this reaction are reported in this note. Since the reaction is fairly rapid at room temperature (25°), the kinetic runs were made at 0°.

Chloramine-T (E. Merck) was purified by the method of Morris *et al.*² and its aqueous solution standardized by the iodometric method. Stock solutions of cinnamyl alcohol (Naarden, b.p. 256.6°) were prepared in 50% aq. ethanol (v/v). A concentrated solution of sodium perchlorate was used to keep the ionic strength constant. All other chemicals used were of analytical reagent grade. The experimental procedure has been described earlier¹.

Stoichiometry—Reaction mixtures containing excess CAT over cinnamyl alcohol in the presence of HCl (overall concentration, 0.5 to 1.0M) were kept at room temperature (25°) for 24 hr. Estimation of the unreacted CAT showed that one mole of cinnamyl alcohol consumed one mole of CAT corresponding to a two electron change. The products were identified as cinnamic aldehyde and *p*-toluenesulphonamide³.

Kinetics of the reaction was studied at several initial [cinnamyl alcohol] and [CAT]. When the

TABLE 1 — EFFECT OF VARYING INITIAL [CINNAMYL ALCOHOL] AND [CHLORAMINE-T] ON RATE CONSTANT

{Solvent: aq. ethanol (50%, v/v); [H⁺]=0.2M; μ=1.0M; temp. = 0°C}

[Chloramine-T] ₀ M	[Substrate] ₀ M	k ₁ × 10 ⁴ sec ⁻¹	[Chloramine-T] ₀ M	[Substrate] ₀ M	k ₁ × 10 ⁴ sec ⁻¹
0.005	0.10	5.114	0.008	0.10	5.048
0.005	0.15	5.318	0.009	0.10	5.178
0.005	0.20	5.230	0.005*	0.10	5.114
0.005	0.30	5.157	0.005†	0.10	5.141
0.005	0.40	5.160	0.005‡	0.10	5.181
0.006	0.10	5.290	0.005**	0.10	5.873
0.007	0.10	5.124	0.005§	0.10	4.984

*In presence of excess *p*-toluenesulphonamide.

†Ionic strength 0.5M.

‡Ionic strength 1.5M.

**Solvent: ethanol-water (60% v/v).

§Solvent: ethanol-water (40% v/v).

TABLE 2 — EFFECT OF VARYING [H⁺] ON THE REACTION RATE

{[Chloramine-T]₀ = 0.005M; [Substrate]₀ = 0.1M; μ = 1.0M; temp. = 0°C}

[H ⁺]M	10 ⁴ k ₁ sec ⁻¹	10 ² k ₁ / [H ⁺] ²	[H ⁺]M	10 ⁴ k ₁ sec ⁻¹	10 ² k ₁ / [H ⁺] ²
0.100	1.237	1.237	0.200	5.114	1.278
0.125	1.996	1.277	0.225	6.466	1.277
0.150	2.806	1.248	0.250	7.809	1.249
0.175	3.823	1.248	0.300	11.150	1.239

TABLE 3 — EFFECT OF VARYING TEMPERATURE ON REACTION RATE

{[Chloramine-T]₀ = 0.005M; [Substrate] = 0.1M; [H⁺] = 0.2M; μ = 1.0M}

Temp. (°K)	k ₁ × 10 ⁴ sec ⁻¹	Temp. (°C)	k ₁ × 10 ⁴ sec ⁻¹
273.0	5.114	282.4	12.12
278.1	8.482	285.5	15.68
280.3	10.710	288.0	20.66

alcohol is in large excess, a plot of log (a/a-x) versus time is found to be linear. The pseudo-first order rate constants (k₁) in CAT are recorded in Table 1. It is found that the reaction is first order with respect to [CAT] and is independent of [substrate]. The reaction rate increases with an increase in [HCl] (0.1 to 0.3M) and the ratio k₁/[H⁺]² is constant (Table 2). Further, a plot of log k₁ versus log [H⁺] is linear with slope 2. Hence the rate of reaction is proportional to [H⁺]².

The thermodynamic parameters were calculated by carrying out the reaction at different temperatures (Table 3). The values are E_a = 57.2 KJ mole⁻¹, Arrhenius factor A = 1.203 ± 0.044 × 10⁹ sec⁻¹; ΔS[‡] = -75.01 ± 0.08 JK⁻¹.

On varying the ionic strength of the medium from 0.5 to 1.5M, the rate constant was unchanged (Table 1). Further, the rate was unaffected by the addition of excess of *p*-toluenesulphonamide (Table 1). The dielectric constant effect on the reaction was followed at different ratios of ethanol-water mixtures and the rate constant increased slightly with the increase in ethanol content (Table 1).

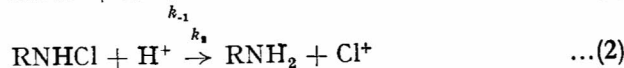
Chloramine-T is a strong electrolyte which dis-

sociates in aqueous solution as



where R = *p*-CH₃C₆H₄SO₂.

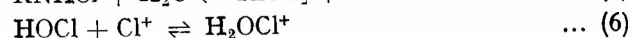
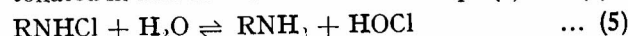
The active chlorine in the compound is assumed to be positive chlorinium ion (Cl⁺) which is formed by a stepwise addition of two protons to the anion RNCl⁻ as follows:



The Cl⁺ ion is only a precursor for the protonated H₂OCl⁺ which could be the oxidizing species in chloramine-T oxidations.



Reaction (2) is assumed to be slowest and rate determining, which also accounts for the absence of any significant effect of RNH₂ on the reaction. The chlorinium ion (Cl⁺) produced in step (2) undergoes hydrolysis by a rapid step to give H₂OCl⁺. This provides an alternate path to the hydrolysis of RNHCl giving rise to HOCl which is subsequently protonated in acid medium as shown in Eqs. (5) and (6).



It is probable that the bypassing of reactions (5) and (6) by (2) and (3) is to be expected in chloraminometric oxidations at higher acid concentrations. Reaction (4) is also a fast step in the oxidation. H₂OCl⁺ can form a chloronium complex of the type C₆H₅CH = CHCH₂OHCIOH₂⁺ with the substrate by a fast step. The complex undergoes a proton abstraction reaction promoted by the π-electron cloud in the substrate leading to the formation of cinnamic aldehyde. Applying steady-state conditions for RNHCl in steps (1) and (2) we get

$$-\frac{d[\text{CAT}]}{dt} = \frac{k_1 k_2 [\text{CAT}][\text{H}^+]^2}{k_{-1} + k_2 [\text{H}^+]}$$

By a consideration of the initial rates of the reaction, the termolecular rate constant k = k₁k₂/k₋₁ is found to be 0.05 litre² mole⁻²sec⁻¹. From this value, k₂ is calculated as 8.5 × 10⁻⁵ min⁻¹. Since k₁ is fairly high, k₋₁ ≫ k₂ [H⁺] would be a reasonable approximation. With this assumption, the rate law becomes

$$-\frac{d[\text{CAT}]}{dt} = k[\text{CAT}][\text{H}^+]^2$$

which is in agreement with the experimental results. The rate of disappearance of CAT is independent of the ionic strength of the medium suggesting an interaction between an ion and a neutral molecule. This is further supported by the small increase in k with the decrease in dielectric constant of the medium and the observed stoichiometry of the reaction.

One of the authors (D.S.M.) is grateful to the UGC, New Delhi, for financial assistance.

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Diamagnetic Susceptibilities of Some Cyclic Dialkylsilylamidoximes

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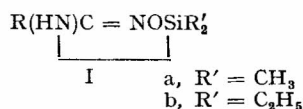
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Received 14 January 1976; accepted 6 March 1976

The diamagnetic susceptibilities of some newly synthesized dialkylsilylamidoximes derived from dialkyl-dichlorosilanes and amidoximes have been determined and found to be in good agreement with calculated values obtained by the method of Baudot. The χ_{Si} and χ_{CH_2} values have also been reported and the lower values of χ_{Si} have been explained on the basis of 'back-bonding'.

DIAMAGNETIC studies have been proved helpful in the interpretation of structural chemistry of silicon¹. The values of χ_{Si} and χ_{CH_2} calculated for a series of silicon compounds containing Si-O bonds have thrown light on the nature of Si-O bonding. However, very little attention was paid to the compounds containing Si-N bond². Very recently diamagnetic studies of trialkylsilylamidoximes³ and dialkylsilyl derivatives of amidoximes⁴ have been reported. In this note experimental and the calculated values of diamagnetic susceptibility of cyclic dialkylsilylamidoximes (containing both Si-O and Si-N bonds) and the values of χ_{Si} and χ_{CH_2} for these series are being reported and discussed.

Precautions were taken to exclude moisture throughout the experimental manipulations. Freshly prepared and purified samples of dialkylsilylamidoximes⁵ (I) were used for the diamagnetic susceptibility measurements. Benzene was used as a reference liquid having specific susceptibility -0.702×10^{-6} cgs units and all the measurements were carried out at room temperature (38°) by Gouy method. For the theoretical value of molecular susceptibility, a wave mechanical method using the concept of bond susceptibility has been employed⁶⁻⁸.



The experimentally determined and the theoretical values for diamagnetic susceptibility are summarized in Table 1 and exhibit fairly good agreement.

The χ_M values for the compounds Ia and Ib ($n = 1, 2, 3$) reported in Table 1 have been treated graphically by plotting molar susceptibility against

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TABLE 1 — DIAMAGNETIC SUSCEPTIBILITY DATA FOR DIALKYL-SILYLAMIDOXIMES (Ia and b)

R	R'	χ_M^* (obs.)	Diff. (%) between obs. and calc.
COMPOUNDS OF THE TYPE Ia			
Me	Me	81.8	-5.2
Et	Me	93.0	-4.8
Pr	Me	105.0	-4.0
Ph	Me	125.4	-1.6
COMPOUNDS OF THE TYPE Ib			
Me	Et	105.0	-4.0
Et	Et	116.0	-3.6
Pr	Et	127.5	-3.2
Ph	Et	148.2	-1.3

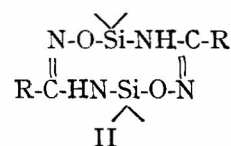
*Numerical values are -10^{-6} cgs units.

TABLE 2 — DIAMAGNETIC SUSCEPTIBILITY OF THE METHYLENE GROUPS AND THE CENTRAL METAL ATOM IN Ia AND Ib

Gradient of plot of χ_M vs n	χ_{CH_2}	Axial intercept	χ_{Si}
COMPOUNDS OF THE TYPE Ia			
11.22	11.22	70.47	17.77
COMPOUNDS OF THE TYPE Ib			
11.26	11.26	93.22	17.80

the length of the alkyl chains in the homologous compounds. Both the plots were linear and the axial intercepts of both give the values of molar susceptibility for the compounds Ia and Ib when $n = 0$. χ_{Si} and χ_{CH_2} (Table 2) have been obtained with the help of these plots using the standard values^{6,9,10}.

The lower values of χ_{Si} (17.77 and 17.80) in comparison to χ_{Si} for Si-C system (reported to be 21.00 for tetra-compounds) is explainable by 'back-bonding' to the silicon atom from oxygen and nitrogen lone-pairs forming ($p \rightarrow d$) π -bonding. These results are consistent with earlier findings for dialkylsilyl derivatives of amidoximes⁴ (systems containing two Si-O bonds). The relatively lower values can be attributed to the lower electronegativity of nitrogen (in comparison to oxygen) permitting relatively stronger π -bonding. Further, these χ_{Si} values are consistent with that for monomeric dialkylsilyl derivatives of amidoximes; supports proposed symmetrical structure (II) for dimeric dialkylsilylamidoximes⁵.



The author wishes to thank the CSIR, New Delhi, for financial support.

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