# Kinetics of nucleophilic substitution reactions of 1-chloromethylnaphthalene with anilines

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**Abstract.** Bimolecular rate constants have been estimated conductometrically for the reaction of 1-chloromethylnaphthalene (1-CMN) with aniline in four solvents to study solvent and temperature effects. The reaction of 1-CMN with various *m*- and *p*-substituted anilines has also been studied in methanol at three temperatures. The results have been analyzed with the help of various empirical relations.

**Keywords.** Hammett relation; Fairclough–Hinshelwood relation; iso-kinetic relation; Dimroth–Reichardt parameter.

## 1. Introduction

The kinetics of the nucleophilic substitution reactions of benzyl chloride have been studied very well (Radhakrishnamurti and Panigrahi 1970; Saksena and Bose 1975; Maccarone *et al* 1977). However, the kinetics of nucleophilic substitution reactions of 1-CMN have not been studied in a systematic manner. This prompted us to investigate the solvent, temperature and nucleophile effects on the kinetics of the nucleophilic substitution reactions of 1-CMN.

## 2. Experimental

### 2.1 *Materials and methods*

1-CMN was prepared by the method reported in the literature (Grumitt and Buck 1943). Solvents were purified by standard methods (Vogel 1978). Anilines were purified by either double distillation over zinc dust or by crystallization. Freshly purified solvents and reagents were used for each kinetic run. The uncertainty in the value of $k$ is of the order of $\pm 2\%$.

### 2.2 *Procedure*

The reaction kinetics were followed by the conductometric method (Patel *et al* 1972). The reaction mixture of required concentration in a particular solvent was prepared by mixing thermostated solutions of 1-CMN (0·02 M) and the appropriate amine (0·04 M). The method of least squares was applied for calculating the rate constant and other parameters.

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### 2.3    *Product analysis*

A solution of 0·2 M 1-cmn and 0·4 M aniline in 100 ml methanol was refluxed for six hours. The solvent was evaporated and the residue treated with anhydrous ether. The anilinehydrochloride which remained insoluble in ether was then removed and the ether was evaporated. The residue remaining after removal of ether was chromato-graphed over silica gel using benzene as eluent. The solid product 1-naphthylmethyl-aniline (yield 90%, m.p. 65°C) was characterized by ir and elemental analysis.

## 3.    Results and discussion

### 3.1    *Effect of nucleophile*

For the reaction of 1-cmn with anilines the values of second order rate constant $k_2$, activation energy $E_a$, Arrhenius frequency factor log $A$, free energy of activation $\Delta G^{\neq}$, enthalpy of activation $\Delta H^{\neq}$ and entropy of activation $\Delta S^{\neq}$ are listed in table 1.

Electron-releasing substituents (-OMe, -OEt, -Me) accelerate the reaction while electron-withdrawing substituents (-Cl, -NO$_2$) retard the reaction.

The Hammett plot was found to be linear at all temperatures. The relation was worked out at 35°C as:

$$\log k_2 = (-0.737)\sigma - 3.541,$$

where $\sigma$ is the substitution constant. The correlation coefficient was estimated to be about 98% at all temperatures. The values of reaction constant, $\rho$, were found to be $-0.737$, $-0.707$ and $-0.639$ at 35, 40 and 45°C respectively. The value of $\rho$ becomes more negative with decrease in temperature. This indicates that the sensitivity of the reaction with anilines to the substituent effect increases with decrease in temperature.

The iso-kinetic relation was worked out at 35°C as:

$$\Delta H^{\neq} = (383.7)\Delta S^{\neq} + 24.51,$$

with correlation coefficient equal to 99·2%. The isokinetic temperature $\beta = 383.7$ K. The applicability of this relationship shows that each reaction in the present series follows the same mechanism *i.e.* $S_{N^2}$ (Leffler 1955).

The Fairclough-Hinshelwood relation (Fairclough and Hinshelwood 1937) was found to be linear. The relation was worked out as:

$$\log A = (-93.12)[1/(E_a)^{1/2}] + 31.19$$

$$\text{(correlation coefficient} = 98.8\%).$$

This indicates that Arrhenius factor $A$ and energy of activation $E_a$ are not independent but linearly related and the present reaction is bimolecular process.

The Bronsted relationship was studied at 35°C. The linear relation was worked out as:

$$\log k_2 = (0.195)pK_a - 4.406$$

with correlation coefficient is equal to 98%.

### 3.2    *Medium effect*

The second order rate constants and kinetic parameters for the reaction of 1-cmn with aniline in different solvent are listed in table 2. The competing solvolysis rates were

**Table 1.** Effect of nucleophile on the rate of reaction in methanol.

| Anilines $pK_a$ ($H_2O$ 35°C) | $k_2 \times 10^4$ (l. mole$^{-1}$ sec$^{-1}$) | | | log A | $E_a$ Kcal. mole$^{-1}$ (KJ. mole$^{-1}$) ($\pm 0.5$) | $\Delta G^{\ddagger}$ (35°) $\pm 0.02$ Kcal. mole$^{-1}$ ($\pm 0.084$ KJ. mole$^{-1}$) | $\Delta H^{\ddagger}$ (35°) $\pm 0.8$ Kcal. mole$^{-1}$ ($\pm 3.35$ KJ. mole$^{-1}$) | $\Delta S^{\ddagger}$ (35°) $\pm 2.2$ cal.deg.$^{-1}$ mole$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| | 35° | 40° | 45° | | | | | |
| p-OMe (5·16) | 5·611 | 9·079 | 13·768 | 9·11 | 17·41 (72·87) | 22·63 (94·68) | 16·81 (70·33) | −18·89 |
| p-OEt (5·05) | 5·049 | 8·211 | 11·940 | 8·51 | 16·62 (69·53) | 22·70 (94·98) | 16·02 (67·03) | −21·65 |
| p-Me (4·90) | 3·266 | 5·173 | 7·973 | 8·43 | 16·78 (70·21) | 22·96 (96·07) | 16·17 (67·66) | −22·01 |
| H (4·45) | 2·464 | 3·724 | 6·095 | 8·89 | 17·62 (73·72) | 23·14 (96·82) | 17·01 (71·17) | −19·92 |
| p-Cl (3·83) | 1·715 | 2·777 | 4·525 | 9·53 | 18·73 (78·36) | 23·35 (97·70) | 18·12 (75·81) | −16·99 |
| m-Cl (3·39) | 1·461 | 2·344 | 3·814 | 9·28 | 18·47 (77·28) | 23·45 (98·12) | 17·87 (74·77) | −18·14 |
| m-NO$_2$ (2·35) | 0·912 | 1·578 | 2·796 | 11·32 | 21·65 (90·58) | 23·74 (99·33) | 21·04 (88·03) | −8·78 |
| p-NO$_2$ (0·93) | 0·839 | 1·433 | 2·533 | 11·01 | 21·25 (88·91) | 23·79 (99·54) | 20·65 (86·40) | −10·22 |

**Table 2.** Medium effect on the rate of reaction.

| Solvent (dielectric constant, $\varepsilon$) | $k_2 \times 10^4$ lit. mole$^{-1}$ sec$^{-1}$ | | | | | $\Delta H^{\neq}$ (35°) ±0·46 Kcal. mole$^{-1}$ (±1·95 KJ. mole$^{-1}$) | $\Delta G^{\neq}$ (35°) ±0·02 Kcal. mole$^{-1}$ (±0·08 KJ. mole$^{-1}$) | $\Delta S^{\neq}$ (35°) ±2·0 Cal. mole$^{-1}$ deg$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| | 30° | 35° | 40° | 45° | 50° | | | |
| Methanol (32·6) | 1·618 | 2·464 | 3·724 | 6·098 | 8·610 | 15·91 (66·57) | 23·14 (96·82) | −23·44 |
| Ethanol (24·3) | 1·059 | 1·611 | 2·512 | 3·917 | 5·546 | 15·73 (65·81) | 23·39 (97·86) | −24·84 |
| Isopropanol (18·3) | 2·187 | 3·111 | 4·842 | 7·430 | 10·789 | 15·17 (63·47) | 22·99 (96·19) | −25·28 |
| n-butanol (17·1) | 0·816 | 1·142 | 1·967 | 3·126 | 4·456 | 16·48 (68·95) | 23·60 (88·74) | −22·97 |
| t-butanol (12·2) | — | 8·261 | — | — | — | — | — | — |

Solvolysis rate $k_1 \times 10^6$ sec$^{-1}$, methanol 3·02; isopropanol 4·21.

found to be extremely negligible compared to $S_{N^2}$ reaction rates (solvolysis rate for methanol and isopropanol are mentioned in the footnote of table 2). Therefore the effect of solvolysis on bimolecular rates can be ignored.

The rate constant of the reaction decreased with the decrease in dielectric constant ($\varepsilon$) of the solvent i.e. the rate of reaction decreases from methanol to ethanol to n-butanol but the rate constant of the reaction in iso-propanol does not fit in this trend. The unusual behaviour observed in isopropanol could be due to the steric effect. In isopropanol, due to the bulk of the solvent reactants, and more particularly anilines, are expected to be very poorly solvated. This probably makes the reagents more reactive and hence the higher rate in isopropanol. This was further supported by studying the same reaction in t-butanol i.e. the rate of reaction was found to be higher than in isopropanol even though the polarity of t-butanol is lower. For the reactions of 1 and 2 naphthacyl bromides with a variety of nucleophiles in aliphatic alcohols similar higher rates in case of isopropanol have been observed (Patel 1982).

The relations between rate constant and some dielectric constant functions like log $\varepsilon$, $\varepsilon - 1/2 \varepsilon + 1$ (Kirkwood's function) and $1/\varepsilon$, were found to be curvilinear (which are not shown here). These are the bulk or macroscopic properties of the medium and do not truly represent the effect of solvent polarity on reaction rates.

The relation between rate constant and Dimroth–Reichardt's, $E_T$ (Reichardt 1965), parameter was found to be linear (the rate constant in isopropanol was not considered due to its unique behaviour). The linear relation was worked out at 50°C as:

$$\log k_2 = (0.0538) E_T - 6.051$$

(correlation coefficient $= 99.3\%$)

### 3.3 Temperature effect

For each reaction the plot of $\log k_2$ against $1/T$ was found to be linear. This shows that each reaction exhibits Arrhenius dependence. The values of energy of activation ($E_a$) free energy of activation ($\Delta G^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$) and entropy of activation ($\Delta S^{\neq}$) listed in tables 1 and 2 are of the same order, observed for other bimolecular nucleophilic substitution reactions. The values of $\Delta G^{\neq}$ are in accordance with the relation given by absolute rate theory ($k = RT/Nh \exp - \Delta G^{\neq}/RT$) i.e. $\Delta G^{\neq}$ decreases with increase in $k_2$. $\Delta S^{\neq}$ is found to be negative as expected for the bimolecular reaction taking place in solution.

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