

## Kinetics of the reaction of alkyl bromides with nucleophiles containing nitrogen atoms

T JANARDHAN RAO, G PUNNAIAH and E V SUNDARAM\*

Department of Chemistry, Kakatiya University, Warangal 506 009, India

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**Abstract.** Kinetics of the reactions of propyl, propargyl and allyl bromides with anilines has been studied in methanol and dipolar DMF. All reactions were found to be of second order. The values of the Bronsted slope (0.4) suggested that bond formation occurs to a considerable extent in the transition state. Electron-donating substituents increased the rate, while electron-withdrawing groups decreased the rate. The magnitudes of the negative values ( $\approx 1$ ) indicate that the reaction rate depends on the availability of electron-density on the nitrogen atom, which implies bond formation, suggesting that all the reactions are  $S_N^2$  in nature, forming a loose transition state. Isokinetic temperature values calculated from the three methods for the reaction of allyl bromide-anilines suggested that the reaction series in DMF is entropy controlled while in a methanol medium hydrogen bonding is responsible for the solute-solvent interactions.

**Keywords.** Kinetics; anilines; alkyl bromides; Hammett relationship; thermodynamic parameters; hydrogen bonding.

### 1. Introduction

The literature survey showed that work on bimolecular nucleophilic substitution reactions of alkyl bromides with anilines is meagre. Particularly, propyl, propargyl and allyl bromides have received little attention. Crocker and Jones (1959), and Panigrahi and Sinha (1977) studied the kinetics of allyl bromide with anilines to some extent but not of propyl and propargyl bromides. Vorob eV (1941) reported that the rate constants for the reaction of pyridineallyl bromide were greater than those of dimethyl aniline-allyl bromide.

Notwithstanding these results, the lack of a systematic investigation of the substituent effect and solvent effect is evident.

Para- and meta-substituted anilines can transmit the electronic effects to the reaction site through their inductance and resonance and this may be different in protic and aprotic solvents. Hence, in the present investigation the effect of the solvents methanol and DMF on the magnitude of the polar substituent effect at 30°C has been studied. The effect of temperature on the reaction of allyl bromide with selected nucleophiles has been studied to evaluate thermodynamic parameters.

### 2. Experimental

The various solid anilines are commercial products which are purified to constant melting points by recrystallisation with aqueous methanol. The liquid anilines were of

\* To whom all correspondence should be addressed.

AnalaR grade and distilled just before the experiment. Allyl bromide (Koch-light), propargyl bromide (Fluka) and *n*-propyl bromide (BDH-AR) were distilled and collected at their respective boiling points. The purity of the compounds was checked by estimating the bromide present in the compound by Volhard's method. Methanol and DMF were purified by standard procedures and used for the experiment.

10 ml of nucleophile (0.02 M) and 10 ml of alkyl bromide (0.02 M) were placed separately in two boiling test tubes and placed in a thermostat for about 15 minutes to attain thermal equilibrium. The two solutions were mixed and a dry conductivity cell was placed in the reaction mixture. The progress of the reaction was followed by measuring the resistance of the reaction mixture using an Elico conductivity bridge type CM-82 T at known intervals of time.

### 3. Results and discussion

All reactions between alkyl bromides and aniline nucleophiles followed second order kinetics, first order each with respect to alkyl bromide and base, proved by the linear plots of  $(R/R - R_\infty)$  versus time. The rate constants calculated by the procedure of Frost and Pearson (1970), were reproducible with an error of  $\pm 2-3\%$ . Rate constants are given in table 1.

#### 3.1 Bronsted relationship

Acid-base strength is used as a model process for correlating nucleophilic reactions not because it is a good model, but mainly because it is a convenient one. Correlations are sought between the logarithm of the rate constant and the  $pK_a$  of the reagent though such correlations are less susceptible to interpretation because the model process and the reaction under study are quite different. In our present study of para- and meta-substituted anilines in the three reaction series, all compounds react quite in consonance with their basicity. A good linear relationship between  $\log k$  and  $pK_a$  is observed in protic methanol and aprotic DMF. From the slopes of the lines the Bronsted coefficients are calculated and recorded in table 1.

The Bronsted coefficient value of about 0.4 in methanol and DMF can be taken to imply that bond formation with the aniline base used occurs to a considerable extent in the transition state.

#### 3.2 Common mechanism

In order to determine whether a common or a different mechanism operates in all the reactions  $\log k$  propargyl bromide is plotted against  $\log k_n$ -propyl bromide.

A fair linear relationship is observed in both the solvents with slopes equal to unity indicating the same mechanism. To confirm this hypothesis, a plot of  $\log k_p$ -anisidine versus  $\log k_p$ -Cl aniline is also drawn. A good linear plot is observed, though only three points on each straight line represent the solvents methanol and DMF. The slopes of these lines are approximately equal to one, implying that all the nucleophiles react by the same mechanism irrespective of different  $\beta$ -carbon hybridization in the substrates.

### 3.3 Substituent effect

Examination of the rate constants that are listed in table 1, reveals that the rate depends on the electron-withdrawing or electron-releasing character of the substituent attached to the aromatic ring. It is evident that the electron-donating substituent in the aniline increases the rate, while electron-withdrawing groups decrease the rate.

A plot of  $\log k$  against  $\sigma$  yielded a straight line. From the slopes of the linear plots of  $\log k$  versus  $\sigma$ , the values of the reaction parameter are calculated and recorded in table 1. The magnitudes of  $\rho$  indicate the susceptibility of alkyl bromides to substituent electronic effects at the reaction site. The observed Hammett correlation (negative slope) indicates that the reaction rate depends on the availability of electron density on the nitrogen atom, which implies bond formation. Further the negative values of  $\rho$  ( $\approx -1$ ) suggest that all the reactions are  $\text{SN}^2$  in nature and form a loose transition state (Ballisteri *et al* 1976; Grob and Schlageter 1977).

### 3.4 Temperature effect

Reactions of all the nucleophiles with allyl bromide are studied in the temperature range 25–45°C in methanol and 30–50°C in DMF. The Arrhenius parameter  $\Delta E$  and the thermodynamic parameters  $\Delta S^\ddagger$ ,  $\Delta H^\ddagger$  and  $\Delta G^\ddagger$  are collected in table 2. Variation of  $\rho$  values has been recorded in table 3.

The isokinetic temperature  $\beta$  has been calculated by the following three methods and computed in table 4: (i)  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$  plot; (ii) Exner's plot; (iii)  $\rho$  temperature relation.

The values of isokinetic parameter  $\beta$  calculated from the above three relations are in good agreement with each other in DMF, but unsynchronised and inconsistent in methanol. This trend unequivocally proves that the reaction series in DMF is entropy controlled. Since the experimental temperature range (303–323° K) is above the isokinetic temperature for the solvent DMF, the increase in magnitude of the negative  $\rho$  values with increase in temperature is a characteristic phenomenon of entropy controlled reactions. Since the  $\rho$  value is insensitive to the variation of temperature in methanol medium, the  $\beta$  value cannot be calculated by the third method.

### 3.5 Solute-solvent interaction

To determine the nature of the reaction series in methanol, the help of Hepler's equation is invoked. Exner's relationship as well as the  $\rho$ - $\beta$  relation failed to provide any conclusion in regard to the nature of the reaction series in methanol. But the conventional isokinetic plot of  $\Delta H^\ddagger$  versus  $\Delta S^\ddagger$  (figure 1) showed the tendency of scatter which is discriminating and characteristic of the nature and position of the groups. This observation together with the ideas put forward by Hepler (1963), Laidler (1959) and Ritchie and Sagar (1964), suggest that if the enthalpy and entropy changes are resolved into external and internal components, a relationship may exist between the external parameters. In this treatment external contributions to enthalpy and entropy are associated with solvent interactions, and internal contributions arise from differences in enthalpy and entropy within the reactant molecules and the transition state. If the reasonable assumption is made that the internal motions of the substituents do not contribute to the free energy, i.e. the internal entropy changes are zero, the

Table 1. Second order rate constants, Bronsted coefficients and reaction constants for the reactions of alkyl bromide with substituted anilines; their  $pK_a$  and  $\sigma$  values in the solvents DMF and MeOH.

| Nucleophile                        | Ionisation constant at 30°C in H <sub>2</sub> O | DMF rate constant $k_2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ |               | MeOH rate constant $k_2 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ |               |                   |       |       |
|------------------------------------|---|---|---------------|--|---------------|-------------------|-------|-------|
|                                    |   | Substituent constant  | Allyl bromide | Propargyl bromide  | Allyl bromide | Propargyl bromide |       |       |
| <i>p</i> -OCH <sub>3</sub> aniline | 5.35  | -0.27   | 813.00        | 457.00   | 23.00         | 169.00            | 79.40 | 4.27  |
| <i>p</i> -CH <sub>3</sub> aniline  | 5.08  | -0.17   | 501.00        | 308.00   | 17.01         | 141.00            | 56.20 | 3.24  |
| Aniline                            | 4.99  | 0.00  | 327.00        | 222.00   | 11.04         | 91.00             | 40.80 | 2.21  |
| <i>m</i> -OCH <sub>3</sub> aniline | 4.20  | 0.12  | 255.00        | 158.00   | 7.80          | 63.00             | 31.60 | 1.78  |
| <i>p</i> -Cl aniline               | 3.98  | 0.23  | 199.00        | 121.00   | 6.31          | 50.00             | 25.80 | 1.42  |
| Bronsted coefficient ( $\alpha$ )  | —   | —   | 0.43          | 0.41   | 0.39          | 0.40              | 0.37  | 0.35  |
| Reaction parameter                 | —   | —   | -1.28         | -1.16  | -1.08         | -1.00             | -0.95 | -0.91 |

[Allyl bromide] = [propargyl bromide] = [nucleophile] = 0.01 M, temperature = 30°C [n-propyl bromide] = [nucleophile] = 0.05 M.

Table 2. Thermodynamic parameters for the reaction of allyl bromide with substituted aniline in the solvents DMF and MeOH at 30°C.

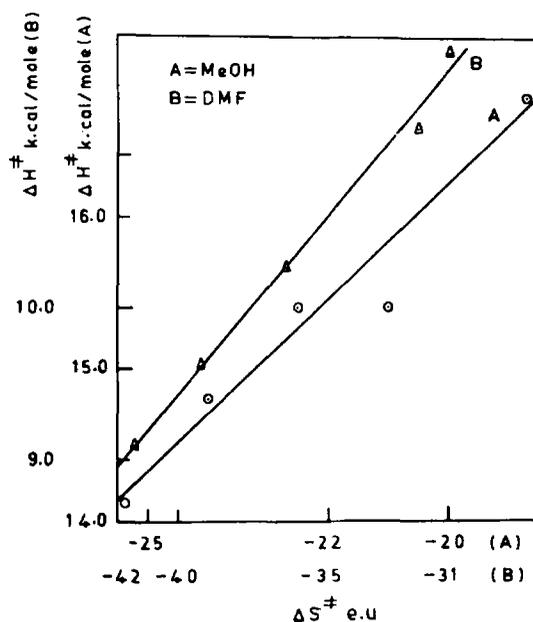
| Substituent                | Second order rate constant at 30°C $k_2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ |       | Activation energy $\Delta E$ kcal/mole |       | Enthalpy of activation $\Delta H^\ddagger$ kcal/mole |       | Entropy of activation $-\Delta S^\ddagger$ e.u. |       | Free energy of activation kcal/mole |       | $\Delta H^\ddagger + 2.303 RT/p\sigma$ kcal/mole (MeOH) |       |
|----------------------------|--|-------|--|-------|--|-------|---|-------|-------------------------------------|-------|---|-------|
|                            | DMF  | MeOH  | DMF                                    | MeOH  | DMF  | MeOH  | DMF   | MeOH  | DMF                                 | MeOH  | DMF   | MeOH  |
| <i>p</i> -OCH <sub>3</sub> | 81.30  | 16.91 | 11.80                                  | 16.00 | 11.19  | 15.40 | 32.00   | 21.00 | 20.00                               | 21.76 | 15.77   | 15.77 |
| <i>p</i> -CH <sub>3</sub>  | 50.10  | 14.10 | 12.30                                  | 14.77 | 11.69  | 14.16 | 31.00   | 25.30 | 21.07                               | 21.84 | 14.39   | 14.39 |
| -H                         | 32.70  | 9.88  | 10.89                                  | 15.43 | 10.28  | 14.82 | 36.40   | 24.00 | 21.30                               | 22.10 | 14.80   | 14.80 |
| <i>m</i> -OCH <sub>3</sub> | 25.50  | 9.51  | 10.22                                  | 16.05 | 9.61   | 15.44 | 39.20   | 22.50 | 21.48                               | 22.27 | 15.20   | 15.20 |
| <i>p</i> -Cl               | 19.90  | 6.31  | 9.70                                   | 17.04 | 9.09   | 16.79 | 41.40   | 18.70 | 21.60                               | 22.40 | 16.47   | 16.47 |

**Table 3.** Variation of  $\rho$  with temperature for the reaction of allyl bromide with substituted anilines in DMF and MeOH.

| Temperature<br>(K) | Reaction constant |       |
|--------------------|-------------------|-------|
|                    | DMF               | MeOH  |
| 303                | -1.28             | -1.00 |
| 313                | -1.35             | -0.97 |
| 323                | -1.42             | -0.98 |

**Table 4.** Different  $\beta$  values for the reaction of allyl bromide with substituted anilines in DMF and MeOH.

| Method  | Value of $\beta$ (K) |      |
|---|----------------------|------|
|   | DMF                  | MeOH |
| $\Delta H^\ddagger$ versus $\Delta S^\ddagger$ plot | 220                  | 360  |
| Exner's plot  | 225                  | 151  |
| $\rho$ -temperature relation                        | 200                  | —    |

**Figure 1.**

following equations (Lee 1963, 1964) may be used as a test of external entropy and enthalpy relationship:

$$\Delta H^\ddagger + 2.303 RT \rho \sigma = b \Delta S^\ddagger$$

where  $\sigma$  is the substituent constant,  $\rho$  is the Hammett reaction constant which is  $-1.0$  at

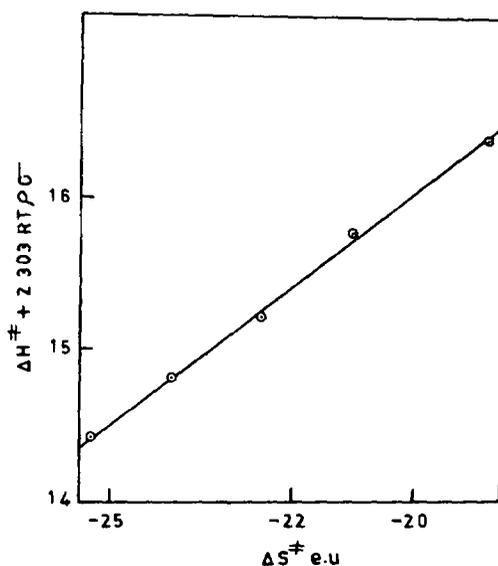


Figure 2.

30°C for the allyl bromide-aniline reaction (table 3),  $b$  is a constant, a characteristic of the reaction, which can be obtained from the slope of a plot of  $\Delta H^\ddagger + 2.303 RT\rho\sigma$  against  $\Delta S^\ddagger$ . The fair linearity of figure 2 unequivocally supports the external contributions to the enthalpy and entropy due to the interactions between the solute and solvent, which may be assumed to arise from the hydrogen bonding between the methanolic proton and the nitrogen atom of the aniline.

### 3.6 Effect of solvent on reaction constant

The effect of the reaction medium on  $\rho$  is also an important factor. This effect may be related to the ease of transmission of electronic effects not only through the molecule but also by a field effect through the solvent. Though the dielectric constants of methanol and DMF are nearly the same, the  $\rho$  value is slightly higher in DMF compared to methanol. The higher values of  $\rho$  in DMF may be partly due to its polarising effect on the electrons of the nucleophile, whereby the substrate can easily discern the nucleophile, thus leading to the higher sensitivity of the reaction, and partly due to the hydrogen bonding in methanol.

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