

## Structure-reactivity correlations in the reactions of phenacyl bromide and ethyl bromoacetate with *ortho*-substituted cinnamate ions

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The second order rate constants in the title reactions in 90% acetone-10% water (v/v) mixture at three different temperatures indicate that electron-releasing substituents accelerate the rate while electron-withdrawing substituents retard the rate. A good Hammett correlation with  $\sigma_p$  constants is obtained for *ortho*-substituted cinnamate ions. The rate data have also been analysed using the method of Charton.

The title investigation has been undertaken as a part of our studies on the reactivity of active halo compounds<sup>1-10</sup>. The effect of *ortho*-substituents on the reactivity of cinnamate ion in the above reactions has been studied using various linear free energy relationships.

### Experimental

All the *ortho*-substituted cinnamic acids were prepared in the laboratory and then purities checked by m.p., TLC analysis and <sup>1</sup>H NMR. Phenacyl bromide was also prepared and purified in the laboratory. Ethyl bromoacetate (E. Merck) and acetone were repeatedly distilled before use.

Kinetic runs were carried out under second order conditions in 90% acetone-10% water (v/v) mixture at 303, 308 and 313K. The second order rate constants were calculated by the method of least-squares. Under the experimental conditions there was no solvolysis of phenacyl bromide and ethyl bromoacetate. The products under the kinetic conditions were identified to be *o*-X C<sub>6</sub>H<sub>4</sub>CH = CHCOOCH<sub>2</sub>COC<sub>6</sub>H<sub>5</sub> (for phenacyl bromides) and *o*-XC<sub>6</sub>H<sub>4</sub>CH = CHCOOCH<sub>2</sub>CO-OC<sub>2</sub>H<sub>5</sub> (for ethyl bromoacetate).

### Results and discussion

The rate data presented in Table 1 show that the rate is accelerated by electron-releasing substituents and retarded by electron-withdrawing substituents in both the reaction series indicating that the reac-

tion rate depends on the electron density of the oxygen atom of the nucleophile. The order of reactivities of the substituents in the above reactions is OMe > Me > H > F > Cl > Br > NO<sub>2</sub> which is the same as that reported for the reactions of phenacyl bromide and ethyl bromoacetate with *para*-substituted cinnamate ions<sup>1,3,7</sup>.

In the *ortho*-substituted cinnamate ions, the reaction site and substituent are not adjacent and hence there should not be any hindrance to the attack of the reagent. This is shown by the satisfactory correlations of the rate data for the two reaction series with  $\sigma_o^*$  substituent constants evaluated by Taft<sup>11</sup> ( $\rho = -0.157$ ;  $r = 0.989$ ;  $s = 0.010$  for the reaction of phenacyl bromide and  $\rho = -0.133$ ;  $r = 0.979$ ;  $s = 0.011$  for the reaction of ethyl bromoacetate).

A good correlation is obtained when log *k* is correlated with  $\sigma_p$  constants in both the reaction series. The  $\rho$  values are  $-0.170$  ( $r = 0.982$ ;  $s = 0.013$ ) and  $-0.148$  ( $r = 0.998$ ;  $s = 0.004$ ) for the reactions of phenacyl bromides and ethyl bromoacetate, respectively with *ortho*-substituted cinnamate ions. The fact that correlation with the Hammett  $\sigma_p$  constants is good shows the absence of steric ef-

Table 1—Second order rate constants and activation parameters for the reaction of *ortho*-substituted sodium cinnamates with phenacyl bromide and with ethyl bromoacetate in 90% acetone-10% water (v/v) mixture

| Substi-<br>tuents                                                                                                            | $10^3 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |       |       | $\Delta H^\ddagger$                | $-\Delta S^\ddagger$                             |
|------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------|-------|-------|------------------------------------|--------------------------------------------------|
|                                                                                                                              | 30°                                                     | 35°   | 40°C  | (kJ mol <sup>-1</sup> )<br>at 35°C | (JK <sup>-1</sup> mol <sup>-1</sup> )<br>at 35°C |
| [ <i>ortho</i> -substituted sodium cinnamate] = 0.01 mol dm <sup>-3</sup> ; [phenacyl bromide] = 0.01 mol dm <sup>-3</sup>   |                                                         |       |       |                                    |                                                  |
| OMe                                                                                                                          | 13.46                                                   | 20.71 | 25.04 | 46.48                              | 126.57                                           |
| Me                                                                                                                           | 12.01                                                   | 19.20 | 23.03 | 48.91                              | 119.29                                           |
| H                                                                                                                            | 11.42                                                   | 17.83 | 22.33 | 50.41                              | 115.02                                           |
| F                                                                                                                            | 10.83                                                   | 16.82 | 22.02 | 53.48                              | 105.56                                           |
| Cl                                                                                                                           | 10.40                                                   | 16.04 | 21.30 | 54.07                              | 104.06                                           |
| Br                                                                                                                           | 10.63                                                   | 16.31 | 20.94 | 50.99                              | 113.89                                           |
| NO <sub>2</sub>                                                                                                              | 8.32                                                    | 13.52 | 16.82 | 53.06                              | 108.74                                           |
| [ <i>ortho</i> -substituted sodium cinnamate] = 0.01 mol dm <sup>-3</sup> ; [ethyl bromoacetate] = 0.06 mol dm <sup>-3</sup> |                                                         |       |       |                                    |                                                  |
| OMe                                                                                                                          | 10.61                                                   | 14.02 | 24.81 | 64.31                              | 91.04                                            |
| Me                                                                                                                           | 9.80                                                    | 13.52 | 23.70 | 66.99                              | 82.68                                            |
| H                                                                                                                            | 9.23                                                    | 12.81 | 22.82 | 68.72                              | 77.49                                            |
| F                                                                                                                            | 8.82                                                    | 12.33 | 22.53 | 71.29                              | 69.45                                            |
| Cl                                                                                                                           | 8.50                                                    | 11.34 | 21.64 | 71.04                              | 70.63                                            |
| Br                                                                                                                           | 8.34                                                    | 11.62 | 21.40 | 71.63                              | 68.83                                            |
| NO <sub>2</sub>                                                                                                              | 7.12                                                    | 9.80  | 18.22 | 71.40                              | 71.00                                            |

fects and secondary bonding in both reaction series. In the absence of steric effect and secondary bonding, Eq. (1) could be derived.

$$C = \frac{\rho_o}{\rho} \dots (1)$$

C represents approximately the electrical effects of a substituent in the *ortho*-position as compared with its electrical effects in the *para*-position<sup>12</sup>. The values of C obtained for the reactions of phenacyl bromide (0.817) and ethyl bromoacetate (0.818) are comparable with the value 0.835, obtained for the ionisation constants of cinnamic acid series in water<sup>12</sup> at 25°C. This shows that *ortho*-substituents in these reactions have the same type of electrical effects as *para*-substituents. The low magnitudes of  $\rho$  obtained in these reaction series (-0.170 and -0.148 for phenacyl bromide and ethyl bromoacetate respectively at 35°C) show that bond breaking has taken place to a greater extent relative to bond making in the transition state. This is contrast to the reactions of phenacyl bromide<sup>13</sup> with benzoate ions ( $\rho = -0.70$ ) and ethyl bromoacetate<sup>2</sup> with benzoate ions ( $\rho = -0.381$ ).

The rate data in the present series were also analysed using Eq. (2) due to Charton<sup>14</sup>.

$$\log k_{ortho} = \alpha\sigma_I + \beta\sigma_R + \phi\nu + h \dots (2)$$

where  $\sigma_I$ ,  $\sigma_R$  and  $\nu$  are the inductive, resonance and steric substituent constants and  $\alpha$ ,  $\beta$  and  $\phi$  are respective coefficients. The results of regression Eq. (2) for the reactions of both phenacyl bromide and ethyl bromoacetate at 35°C are given by the correlation Eqs (3) and (4), respectively.

$$\log k_{35} = -0.207 \sigma_I - 0.190 \sigma_R + 0.029 \nu - 1.755 \\ (\pm 0.025) (\pm 0.023) (\pm 0.017) \dots (3)$$

R = 0.992; SE = 0.010; n = 7; CL = 99.9%; F = 64.09

$$\log k_{35} = -0.156 \sigma_I - 0.143 \sigma_R + 0.001 \nu - 2.89 \\ (\pm 0.009) (\pm 0.008) (\pm 0.006) \dots (4)$$

R = 0.999; SE = 0.004; n = 7; CL = 99.9%; F = 364.3

The significance of the correlation was tested by means of the F-test and the significance of the various contributing terms was tested by means of the t-test. The confidence levels of the t-test for the significance of inductive and resonance terms are above 90% and that for the steric term is below 90% indicating that the inductive and resonance effects are important in these reaction series.

The values of isokinetic temperatures are found to be 342K and 335K for the reactions of phenacyl bromide and ethyl bromoacetate with cinnamate ions respectively. The plots of  $\log k_{40^\circ}$  versus  $\log k_{30^\circ}$  are linear ( $r = 0.984$ ;  $s = 0.010$  for phenacyl bromide and  $r = 0.982$ ;  $s = 0.009$  for ethyl bromoacetate) indicating the operation of one and the same mechanism in the given reaction series.

Brönsted-type of correlations between  $\log k_2$  and  $pK_a$  ( $\beta = 0.232$ ;  $r = 0.945$ ;  $s = 0.088$  and  $\beta = 0.189$ ;  $r = 0.898$ ;  $s = 0.116$  at 308 K respectively) of the conjugate acid of the nucleophile in the reactions of phenacyl bromide and ethyl bromoacetate with *ortho*-substituted cinnamate ions are fair. The positive values of the Brönsted coefficient in the two reaction series point out that the rate increases with increasing basicity of the nucleophile. The magnitude of  $\beta$  in these reaction series suggests that there is little bond formation between oxygen atom of the carboxylate ion and central carbon atom containing the bromine.

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#### References

- 1 Srinivasan C, Shunmugasundaram A & Arumugam N, *Indian J chem*, 20B (1981) 467.
- 2 Srinivasan C, Shunmugasundaram A & Arumugam N, *Indian J chem*, 20B (1981) 1057.
- 3 Srinivasan C, Shunmugasundaram A & Arumugam N, *Indian J chem*, 21B (1982) 355.
- 4 Srinivasan C, Shunmugasundaram A & Arumugam N, *Indian J chem*, 21B (1982) 662.
- 5 Srinivasan C, Shunmugasundaram A & Arumugam N, *J chem Soc, Perkin-II* (1984) 213.
- 6 Srinivasan C, Shunmugasundaram A, Roja M & Arumugam N, *Indian J chem*, 23B (1984) 555.
- 7 Srinivasan C, Shunmugasundaram A & Arumugam N, *J chem Soc, Perkin-II* (1985) 17.
- 8 Shunmugasundaram A & Balakumar S, *Indian J chem*, 24A (1985) 775.
- 9 Shunmugasundaram A & Rajakumar M, *Indian J chem*, 25A (1986) 71.
- 10 Shunmugasundaram A & Radhakrishnan K, *Indian J chem*, 26A (1987) 827.
- 11 Taft R W, in *Steric effects in organic chemistry*, (Wiley, New York) (1956) Ch. 13.
- 12 Charton M, *Can J chem*, 38 (1960) 2493.
- 13 Mishra P, Nayak P L & Rout M K, *Indian J chem*, 11 (1973) 452.
- 14 Charton M, *Prog phys org chem*, 8 (1971) 235.