

Reaction of ethyl bromoacetate with substituted naphthoate ions

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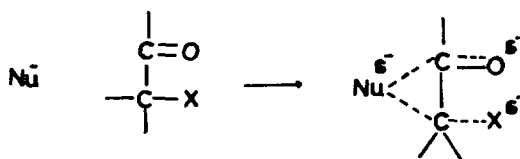
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Abstract. Rate constants for the reaction of ethyl bromoacetate with three series of substituted naphthoate ions have been measured in an acetone-water mixture (90% v/v). Using σ_p values rate constants at 30° correlate well with the Hammett equation yielding $\rho = -0.54, -0.19$ and -0.25 for (4, 1-), (6, 1-) and (6, 2-) series, respectively. Comparison of these ρ values with those of the reaction of phenacyl bromide reveals the failure of the reactivity-selectivity principle RSP in these reactions. Failure of RSP has been explained in terms of isoselective temperature.

Keywords. Ethyl bromoacetate; substituted naphthoate ions; Hammett equation; reactivity-selectivity principle; isoselective relationship.

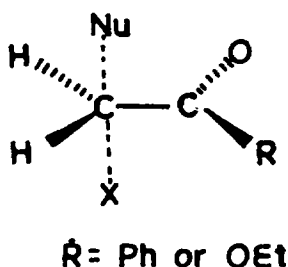
1. Introduction

The reactivities of α -halo ketones and α -halo esters towards nucleophilic reagents have been subjects of investigation over several decades. The reaction between α -halo compounds and nucleophiles is a simple S_N2 reaction. The formation of intermediates in these reactions has been ruled out by Thorpe and Warkentin (1973). Various mechanisms have been proposed to explain the activation caused by the α -carbonyl group. Dewar (1949) first suggested that the α -carbonyl group stabilises the transition state through resonance delocalisation and that the partial $\text{Nu} \cdots \text{C}$ and $\text{C} \cdots \text{X}$ bonds must be necessarily aligned with the π -plane of the carbonyl group so that the excess negative charge on the central carbon can be delocalised into the π^* molecular orbital. This was supported by Bordwell and Brannen (1964). In a variation of this idea, Winstein *et al* (1951) postulated that delocalisation could be assisted by bridging of the nucleophile between the α -carbon and the carbonyl carbon in the transition state as shown in scheme 1. In contrast, Pearson *et al* (1952) invoked an electrostatic effect to explain the α -carbonyl enhancement. The carbonyl group induces an electron deficient centre at the carbon with the halogen atom, thereby attracting the nucleophile towards



Scheme 1

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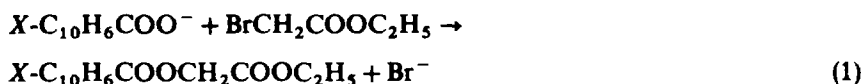


itself. Experiments conducted by Thorpe and Warkentin (1973) suggest that electrostatic effects are not the major reason for the rate enhancement. Evidence indicating a definite geometric requirement in the transition state was furnished by Bartlett and Trachtenberg (1958). Theoretical calculations conducted on the S_N2 transition state by Wolfe *et al* (1982) and Kost and Aviram (1982) indicate a perpendicular geometry for the transition state as shown below. It is only in such an arrangement that the developing partial negative charge on the α -carbon can be effectively delocalised into the π^*_{CO} orbital (consistent with Dewar mechanism) or the nucleophile undergo partial interaction with the carbonyl group leading to bridging (as in the Winstein scheme).

Although the kinetics of the reactions of α -haloketones with different kinds of nucleophiles have been studied, relatively little attention has been paid towards the reactivity of α -haloesters. In this paper, we report our investigations on the S_N2 kinetics of ethyl bromoacetate (EBA) with several substituted naphthoate ions.

2. Results and discussion

The reaction between EBA and the naphthoate ion follows second order kinetics and can be represented by (1).



The products were found to be exclusively naphthoylglycolates, as characterised by their analytical data (table 1). The bimolecular rate constants for the reaction of EBA with several substituted naphthoate ions are given in table 2.

The second order rate constants for the reaction of 1-naphthoate ion with phenacyl bromide (PB) and EBA are respectively $2.78 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Rajasekaran and Gnanasekaran 1982) and $2.48 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (table 2) at 35° . These values show that EBA is less reactive than PB. The electron withdrawing ability of the carboxy group is greater than that of the carbonyl group. Based on electronic effects alone it may be expected that EBA should react at a faster rate than PB if the activation caused by the α -carbonyl group is only due to inductive electron withdrawal as suggested by Pearson *et al* (1952). But the experimental results are quite contrary to this expectation and this suggests that the electrostatic effects are not the major reason for the rate enhancement of the reaction of α -halocompounds.

The rate data (table 2) indicate that electron-attracting substituents in the naphthalene ring decrease the rate while electron-releasing substituents increase it. The

Table 1. Analytical data.

Substituent	m.p. (°C)	Molecular formula	Observed (%)		Required (%)	
			C	H	C	H
<i>Ethyl 4-substituted 1-naphthoyleglycolates</i>						
H	35	C ₁₅ H ₁₄ O ₄	70.0	5.0	69.8	5.4
F	64	C ₁₅ H ₁₃ O ₄ F	65.1	4.9	65.2	4.7
Cl	43	C ₁₅ H ₁₃ O ₄ Cl	61.7	4.6	61.6	4.4
CH ₃	59	C ₁₆ H ₁₆ O ₄	70.4	6.0	70.6	5.9
NO ₂	216	C ₁₅ H ₁₃ O ₆ N	59.5	4.0	59.4	4.2
<i>Ethyl 6-substituted 2-naphthoyleglycolates</i>						
H	76	C ₁₅ H ₁₄ O ₄	69.9	5.8	69.8	5.4
F	61	C ₁₅ H ₁₃ O ₄ F	65.4	4.9	65.2	4.7
Br	99	C ₁₅ H ₁₃ O ₄ Br	53.4	4.0	53.4	3.9
CN	91	C ₁₆ H ₁₃ O ₄ N	67.6	4.5	67.8	4.6
CH ₃	88	C ₁₆ H ₁₆ O ₄	70.5	6.1	70.6	5.9
OCH ₃	82	C ₁₆ H ₁₆ O ₅	66.8	5.7	66.7	5.6

Table 2. Rate constants for the reaction of ethyl bromoacetate with substituted naphthoate ions in 90% (v/v) acetone-water mixture.

Substituent	10 ⁴ k mol ⁻¹ dm ³ s ⁻¹			E _a kJmol ⁻¹	ΔH [‡] kJmol ⁻¹	-ΔS [‡] JK ⁻¹ mol ⁻¹
	30°	35°	40°			
<i>Sodium 4-substituted 1-naphthoates</i>						
OMe	21.0	28.9	41.6	51.9	49.4	132.2
CH ₃	19.6	26.6	38.0	53.5	51.0	128.4
H	16.3	24.8	36.3	56.9	54.4	118.8
F	15.0	22.5	32.4	59.4	56.9	111.3
Cl	12.3	16.6	26.9	61.1	58.6	107.5
Br	12.3	16.2	26.4	61.1	58.6	107.5
NO ₂	5.8	9.6	14.2	70.3	67.8	83.3
<i>Sodium 6-substituted 1-naphthoates</i>						
OMe	17.4	25.2	37.0	59.0	56.5	111.3
CH ₃	16.8	25.0	36.9	61.5	59.0	103.4
Cl	14.0	22.0	32.0	64.8	62.3	94.1
Br	14.0	22.0	32.0	64.8	62.3	94.1
CN	11.6	18.2	27.0	66.5	64.0	90.0
<i>Sodium 6-substituted 2-naphthoates</i>						
OMe	10.0	17.0	25.0	74.5	72.0	65.7
CH ₃	9.4	16.5	24.0	75.3	72.8	62.8
H	8.6	15.6	22.8	76.6	74.1	59.4
F	7.8	14.2	21.5	79.5	77.0	50.6
Cl	7.4	13.7	20.9	81.6	79.1	43.9
Br	7.4	13.7	20.9	81.6	79.1	43.9
COMe	6.2	12.5	19.2	85.3	82.8	33.1
CN	6.0	11.2	17.8	88.7	86.2	22.2

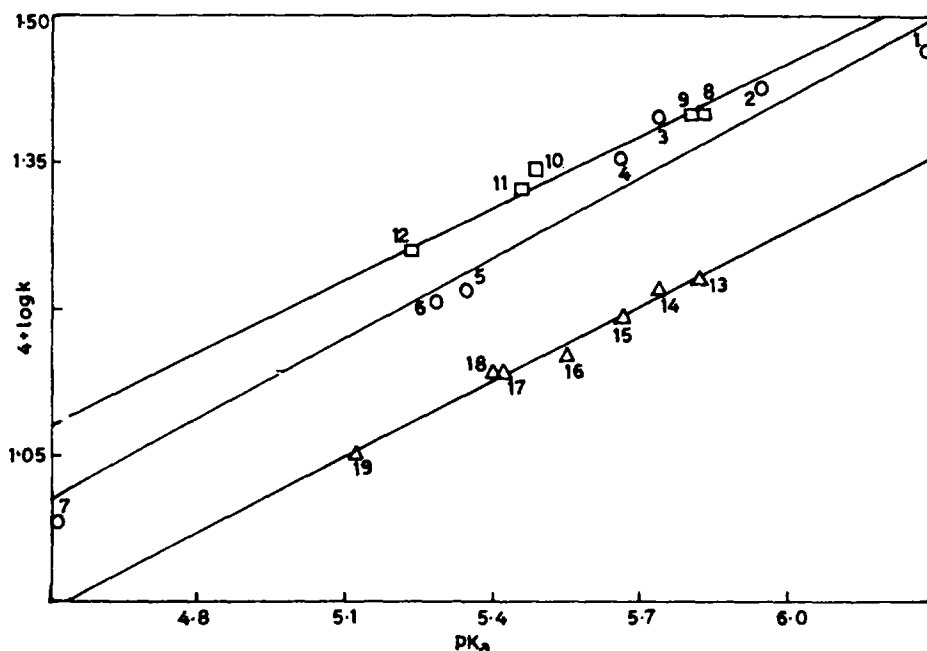


Figure 1. Brønsted plot for the reaction of EBA with substituted naphthoate ions. O: 4, 1-series; □: 6, 1-series; Δ: 6, 2-series.

rate of the reaction depends on the electron density on the oxygen atom of the carboxylate ion. The logarithm values of the rate constants are found to be linearly related to the pK_a of the corresponding naphthoic acids (figure 1). The Brønsted coefficients, α , are found to be 0.32, 0.28 and 0.28 for the (4, 1-), (6, 1-) and (6, 2-) series respectively at 35°. The smaller α values indicate little bond formation in the transition state (Mohanty and Nayak 1975).

The values of activation energy show a regular variation with nature of substituents; electron-attracting substituents increase and electron-releasing substituents decrease the activation energy. The entropies of activation are negative as expected for bimolecular reactions. The plots of ΔH^\ddagger versus ΔS^\ddagger are linear for all the three series. The linear relationship between ΔH^\ddagger and ΔS^\ddagger is indicative of a single mechanism operating throughout the series (Bowden *et al* 1964).

The rate data for the reaction of EBA with substituted naphthoate ions have been correlated with σ_p constants (table 3) and, for comparison, the rate data for the reaction of PB with naphthoate ions (Baliah and Ananthakrishna Nadar 1977; Ananthakrishna Nadar and Gnanasekaran 1975; Rajasekaran and Gnanasekaran 1982) have also been correlated with σ_p constants (table 3). Good correlations were obtained in all cases. Examination of the data in table 3 shows that the magnitude of ρ is nearly equal for the reaction of PB and EBA for all the three series studied.

For a family of linear free energy relationships, substrates $x_1, x_2 \dots x_n$ reacting with reagents $y_1, y_2 \dots y_m$, the selectivity denoted by ρ will decrease as the rate increases, if the reactivity-selectivity principle (RSP) is in operation (Hammond 1955). In spite of the

Table 3. Hammett reaction constants for the reaction of EBA and PB with naphthoate ions.

System	Reactant	Temperature (°C)	ρ	r	s
4,1-	EBA	30	-0.54 ± 0.01	0.993	0.017
4,1-	EBA	35	-0.48 ± 0.02	0.972	0.031
4,1-	EBA	40	-0.45 ± 0.03	0.979	0.041
4,1-	PB	30	-0.59 ± 0.03	0.980	0.042
4,1-	PB	35	-0.56 ± 0.03	0.984	0.038
6,1-	EBA	30	-0.19 ± 0.01	0.991	0.009
6,1-	EBA	35	-0.15 ± 0.01	0.980	0.013
6,1-	EBA	40	-0.15 ± 0.01	0.980	0.012
6,1-	PB	30	-0.17 ± 0.01	0.983	0.011
6,1-	PB	35	-0.15 ± 0.01	0.970	0.014
6,2-	EBA	30	-0.25 ± 0.02	0.981	0.015
6,2-	EBA	35	-0.19 ± 0.01	0.991	0.009
6,2-	EBA	40	-0.15 ± 0.01	0.994	0.005
6,2-	PB	30	-0.39 ± 0.04	0.925	0.039
6,2-	PB	35	-0.21 ± 0.01	0.987	0.009

fact that EBA is less reactive than PB, the ρ values for the two reactions are almost the same and this indicates the failure of RSP in these reactions.*

When plots of selectivity $\log(k_{PB}/k_{EBA})$ versus $\log(k_{PB})_{rel}$ are made for the (4, 1-) and (6, 2-) series at 35°, all the substituents show almost the same selectivity. The selectivity will depend on temperature (Geise 1977) according to (2) if the competing reactions have different activation enthalpies.

$$\log k_2/k_1 = [(\Delta H_2^\ddagger - \Delta H_1^\ddagger)/2.303 RT] - [(\Delta S_2^\ddagger - \Delta S_1^\ddagger)/2.303 R] \quad (2)$$

The selectivity values will coincide at the isoselective temperature (T_{iso}), i.e. $\delta \log k_2/k_1 = 0$ and hence (2) reduces to (3).

$$[\delta(\Delta H_2^\ddagger - \Delta H_1^\ddagger)/2.303 RT_{iso}] - [\delta(\Delta S_2^\ddagger - \Delta S_1^\ddagger)/2.303 R] = 0. \quad (3)$$

Equation (3) can be rearranged as follows:

$$\delta(\Delta H_2^\ddagger - \Delta H_1^\ddagger) = T_{iso} \delta(\Delta S_2^\ddagger - \Delta S_1^\ddagger). \quad (4)$$

Thus the isoselective temperature can be obtained from the slope of the plot of $\delta(\Delta H_2^\ddagger - \Delta H_1^\ddagger)$ versus $\delta(\Delta S_2^\ddagger - \Delta S_1^\ddagger)$.

If the variation of the reactants x_m or the partners y_n can be described by linear free energy relationships, the reaction parameters of the individual series of reaction series are essentially equal at the isoselective temperature. The RSP is applicable only above or

* The referees have pointed out that "the breakdown of RSP is meaningful only for reactions proceeding by the same mechanism and this may not be the case in the systems studied, because carbonyl participation is conceivable for the reactions of PB but not for those of EBA. Also, the magnitude and variation in ρ values are too small to make a strong case for the failure of RSP. Finally, the most systematic way of examining the problem would be by studying the rate for different nucleophiles". Assuming that the failure of RSP is indeed significant, we have made an attempt to rationalize the available data on the basis of the concept of isoselective temperature.

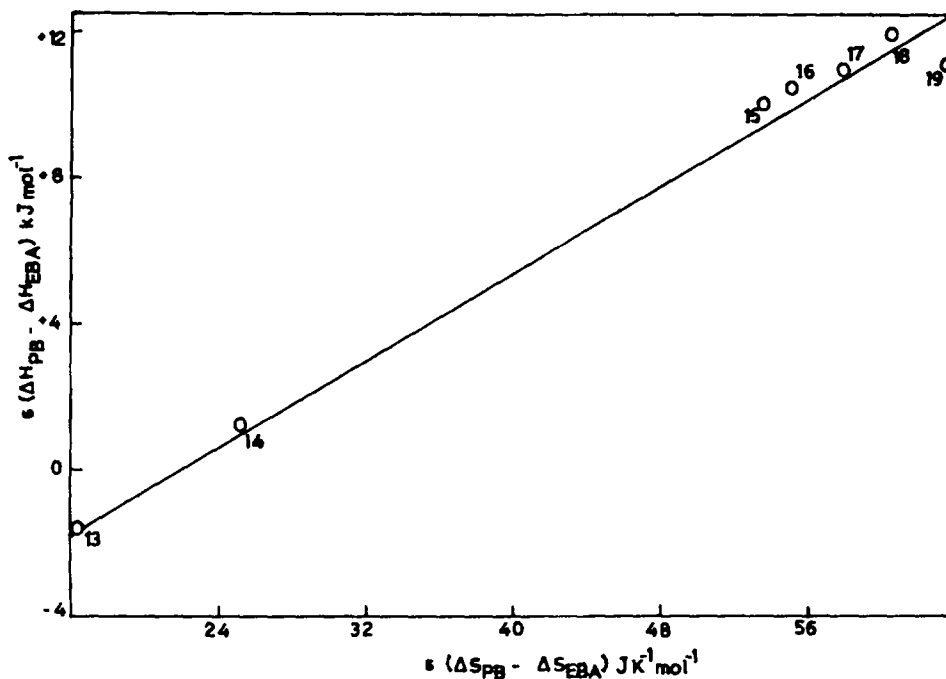


Figure 2. Plot of $\delta(\Delta H_{PB}^\ddagger - \Delta H_{EBA}^\ddagger)$ versus $\delta(\Delta S_{PB}^\ddagger - \Delta S_{EBA}^\ddagger)$ for 6, 2-series. ΔH_{PB}^\ddagger and ΔS_{PB}^\ddagger are from Ananthakrishna Nadar and Gnanasekaran (1975).

below the isoselective temperature (Giese 1977). A plot of $\delta(\Delta H_{PB}^\ddagger - \Delta H_{EBA}^\ddagger)$ versus $\delta(\Delta S_{PB}^\ddagger - \Delta S_{EBA}^\ddagger)$ is linear (figure 2; $r = 0.990$; $n = 7$) for the (6, 2-) series and from the slope, the isoselective temperature is found to be 20° . A similar plot for the (4, 1-) series ($r = 0.997$; $n = 7$) yields the isoselective temperature as 40° . The experimental and the isoselective temperatures are close to each other. This may be the possible cause for the failure of RSP in these reactions.

3. Experimental

All the naphthoic acids were prepared as described by Ananthakrishna Nadar and Gnanasekaran (1978) and converted into sodium salts. Acetone was purified by standard methods and the course of the reaction was followed by estimating the amount of bromide ion formed, by Volhard's method.

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