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Ortho-Effect on Reaction of Triethylammonium *Ortho*-Substituted Benzoates with Phenacyl Bromide

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The kinetics of the reaction of phenacyl bromide with *ortho*-substituted benzoic acids in the presence of triethylamine at 25°, 30° and 35°C in acetone have been studied. The reaction follows second order kinetics, first order with respect to phenacyl bromide and first order with respect to carboxylate. The attacking nucleophile is assumed to be triethylammonium benzoate ion-pair. Electron-releasing groups accelerate the reaction, while electron-withdrawing groups retard the reaction. The large negative entropy of activation indicates a rigid cyclic transition state. The existence of isokinetic relationship indicates that the same mechanism operates in the whole series. The rate data do not obey Bronsted relationship; the Taft's polar substituent constants and inductive effects of the *ortho*-substituents are found to be insignificant. The steric factors of the *ortho*-substituents are found to be less important while the resonance effect for this system is found to be more important in the reaction series.

INTRODUCTION

The nature of the *ortho*-effect and the attempts to correlate *ortho*-substituent effects to *ortho*-substituent constants lead to much diversified views$^{1-15}$. There is often poor agreement between the various values evaluated for the *ortho*-substituent constants of a given substitutent and rate constants. Moreover, in certain situations a particular series is subjected to unexpected steric or other unknown interference from the *ortho*-substituents. There is also a paucity of experimental data on the titled compounds unlike in the case of *para*- and *meta*- series. With a view to analyzing the nature of the *ortho*-effect further, the kinetics of reaction between phenacyl bromide and a number of *ortho*-substitued benzoic acids in acetone were carried out.

RESULTS AND DISCUSSION

The second-order rate constants of various *ortho*-substituted benzoic acids with phenacyl bromide in the presence of triethylamine have been determined at 25°, 30° and 35°C in acetone and are presented in Table-1. An analysis of the data

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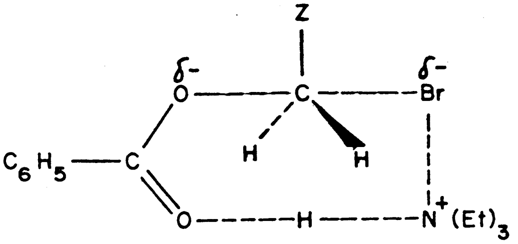
TABLE-1
SECOND-ORDER RATE CONSTANTS FOR THE REACTION OF PHENACYL BROMIDE WITH *ORTHO*-SUBSTITUTED BENZOIC ACIDS IN THE PRESENCE OF TRIETHYLAMINE IN ACETONE

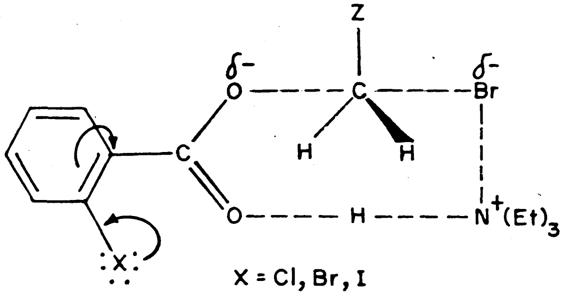
S. No.	Substitutent	$k_2 \times 10^2$ dm^3 mol^{-3} s^{-1}		
		25°C	30°C	35°C
1.	Br	1.63	2.14	2.77
2.	I	1.60	1.96	2.58
3.	Cl	1.55	2.07	2.42
4.	CH_3	1.37	1.93	2.53
5.	H	1.18	1.56	2.22
6.	NO_2	0.73	0.94	1.44
7.	OCH_3	0.70	0.90	1.14

shows that the halogens and methyl group accelerate the reaction and the nitro and methoxyl group decelerate the reaction. The behaviour of various substituents in this series can be explained as follows. A cyclic transition state as shown in Fig. 1 has been visualised for the reaction between triethylammonium benzoate and phenacyl bromide[16]. The halogens in the *ortho* position accelerate the reaction. The lone pair of electrons on the halogens may be delocalised as shown in Fig. 2. The delocalisation may bring about electron flown from the benzene



$Z = C_6H_5CO-$

Fig. 1



$X = Cl, Br, I$
$Z = C_6H_5CO-$

Fig. 2

ring to the carboxylate carbon, which may result in an increase of electron density on the oxygen. The *ortho*-methyl group may also increase the electron density in the transition state in the same manner by its electron-releasing inductive effect. The *ortho*-nitro group, by its electron-attracting mesomeric and inductive effects reduces the electron density on the oxygen atom of the carbonyl group in the transition state and hence retards the reaction. The *ortho*-OCH_3 group behaves differently. It should have facilitated the reaction by its electron releasing inductive effect. There are ample experimental evidences and theoretical conclusions to prove that an *ortho*-substituent to methoxyl groups makes it mores planar to benzene ring increasing the conjugation. This phenomenon is also termed as steric enhancement resonance[17, 18]. But actually the reaction is retarded. It can be explained on the basis of internal hydrogen bonding with the reaction centre as shown in Fig. 3 resulting in a decrease in the electron density in the carboxyl function. The idea of internal hydrogen bonding of the *o*-OMe group is supported by the various reports in literature[13, 19, 20]. From the experimental data the *ortho*-substituents can be arranged in the decreasing order of reactivity as follows:

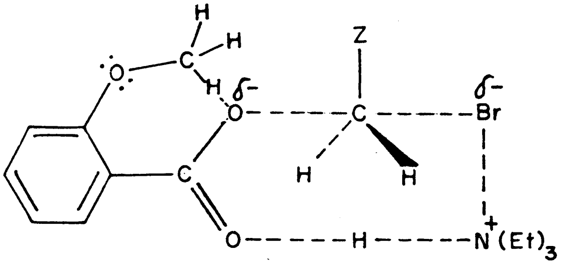


Fig. 3

$$Br > I > Cl > CH_3 > H > NO_2 > OCH_3$$

The rate constants measured at 35°C for the reaction of phenacyl bromide with *ortho*-substituted and *para*-substituted benzoic acids are compared in Table-2. The data show that electron-releasing substituents act as retarders while halogens and electron-withdrawing substituents like —NO_2 act as accelerators for the reaction in the case of *p*-substituted benzoic acid. This is contrary to expectations[5, 6, 7, 21]. This may be due to the fact that the reaction runs have been carried out at a temperature above the isokinetic temperature[22, 23].

In the present case, the electron-releasing groups, except —OMe, accelerate the reaction while the electron-withdrawing group, —NO_2, retards. This is in agreement with the expectation because the reaction temperatures is below the isokinetic temperature whereas the substitutent effects are normal. Thus halogens behave similarly in both the cases. This behaviour of halogens could be explained only if it is assumed that the coplanarity of the benzene ring and halogens is not destroyed due to any steric factor between the *ortho*-substituent and the reaction site, which facilitates some sort of delocalisation of the lone pair of electrons on halogens.

TABLE-2
COMPARISON OF RATE CONSTANTS OF *ORTHO*- AND *PARA*-SUBSTITUTED BENZOIC ACIDS WITH PHENACYL BROMIDE

S. No.	Substituent	$k_2 \times 10^2$ dm^3 mol^{-3} s^{-1} 35°C	
		Para	*Ortho*
1.	Br	2.57	2.77
2.	I	2.46	2.58
3.	Cl	2.82	2.42
4.	CH_3	1.89	2.53
5.	H	2.22	2.22
6.	NO_2	2.36	1.44
7.	OCH_3	1.73	1.14

The plot between the rates and pK_a values (Table-3) is not linear indicating the failure of Bronsted relationship[24]. This failure may be due to different effects on *ortho*-substituents separately influencing the rate and acidity. Moreover, basicity is thermodynamically controlled and reactivity is kinetically controlled[25].

TABLE-3
pK_a VALUES AND RATE DATA OF *ORTHO*-SUBSTITUTED BENZOIC ACIDS

S. No.	Substituent	pK_a	$\log k_2$
1.	Br	–1.5571	2.84
2.	I	–1.5889	2.85
3.	Cl	–1.6155	2.92
4.	CH_3	–1.5971	3.91
5.	H	–1.6542	4.19
6.	NO_2	–1.8428	2.16
7.	OCH_3	–1.9416	4.47

The activation parameters are presented in Table-4. The electron-donating substituents and the halogens have lower energy of activation, whereas nitro group has a higher value for energy of activation. All the benzoic acids, except *o*-nitrobenzoic acid, have lower frequency factor (PZ) compared to benzoic acid itself. The enthalpy of activation shows a regular variation in that electron-donatng substituents and the halogens decrease $\Delta H^{\#}$, whereas the nitro group increases. In general, this series is manifested by high negative entropy of activation. A greater crowding in the transition state is mainly responsible for a higher rigid transition state leading to considerable decrease in entropy. On this basis, a cyclic transition state as shown in Fig. 1 has been visualised for the reaction between triethylammonium benzoates and phenacyl bromide.

TABLE-4
ACTIVATION PARAMETERS FOR THE REACTION OF PHENACYL BROMIDE WITH *o*-SUBSTITUTED BENZOIC ACIDS

S. No.	Substituent	E_a kJ mol^{-1}	$\Delta H^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ e.u.	log PZ
1.	Br	41.00	38.49	35.8	5.4
2.	I	36.40	33.89	39.6	4.6
3.	Cl	38.49	35.98	38.0	4.9
4.	CH_3	46.44	44.35	31.5	6.3
5.	H	48.12	45.60	30.8	6.5
6.	NO_2	52.30	49.79	28.4	7.0
7.	OCH_3	37.24	34.73	40.5	4.3

In the transition state, it is shown that the methylene carbon of phenacyl bromide is subjected to SN_2 reaction by the oxygen of the hydrogen-bonded benzoate and the bromide atom is being pulled out as triethylammonium bromide. In view of the rigid orientation that the substrate and the reagent should take, the number of energy levels available to the transition state relative to the ground state is reduced and $\Delta S^{\#}$ becomes more negative[16]. The linear plot between $\Delta H^{\#}$ and $\Delta S^{\#}$ (Table-4, Fig. 4) signifies that the same mechanism operates in the

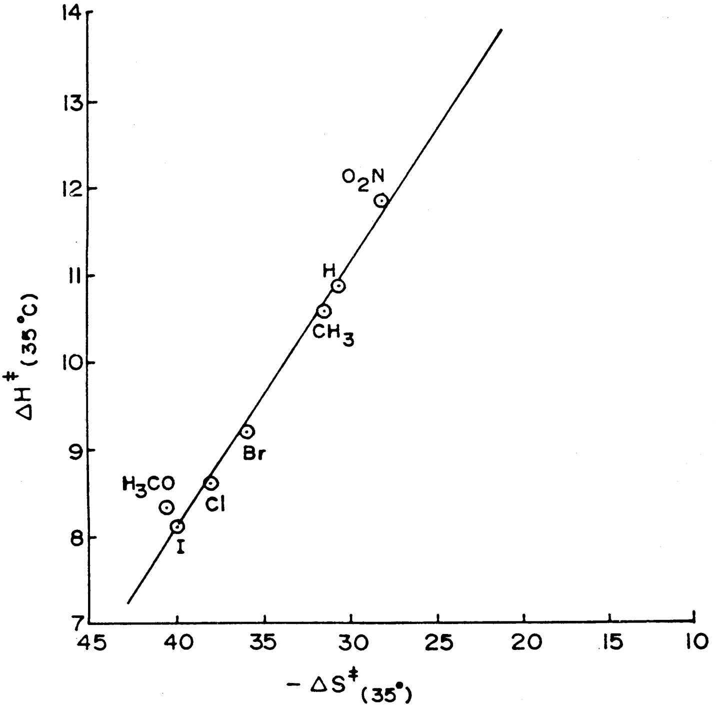


Fig. 4. Plot of $\Delta H^{\dagger}$ at 35°C *vs.* $\Delta S^{\ddagger}$ at 35°C

whole series[26, 27]. The isokinetic temperature has been determined by plotting log k_2 at 35°C *vs.* log k_2 at 30°C and the temperature is found to be equal to 323 K. Due to some practical constraints we were able to make kinetic measurements only at the temperatures reported. Our reaction temperatures are below the isokinetic temperature so that substituent effects on rate constants are anticipated.

A poor correlation (r = 0.854) between log (log k/k_H) or log (k/k_{CH}) and E_s^o, the steric parameter of the *ortho*-substituents indicates that the steric factor does not play any significant role in this series. There is no correlation between log (k/k_H) at 35°C and σ^o, the Taft substituent constant, or σ_x, the inductive substituent constant, showing that these factors are insignificant as far as this reaction series is concerned. When log (k/k_H) at 35°C is plotted against σ^o, the resonance substituent constant, a poor correlation (r = 0.879) is obtained. But when log (k/k_H) at 35°C is plotted against σ^n the resonance substituent constant for insulated system correlation (r = 0.896) is better. These factors show that the Hammett resonance substituent constant is the most significant of all other factors in this reaction series.

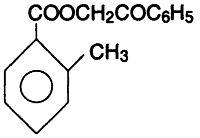
EXPERIMENTAL

Benzoic acid analytical grade was used as such. *o*-Chloro-, *o*-bromo-, *o*-iodo-, *o*-methoxy-, *o*-nitro benzoic acids, *o*-toluic acid and phenacyl bromide were prepared by standard methods and purified until constant m.p. was obtained.

Rate measurements: The reactions were carried out in dry acetone (BDH AnalaR used as such). The thermostatted (±0.01°C) solution of phenacyl bromide (25 mL, 0.05 mol dm^{-3}) in acetone were mixed. The course of the reaction was followed by pipetting out 5 mL aliquots of the reaction mixture at different intervals of time, adding it to 10 mL of (0.025 mol dm^{-3}) silver nitrate solution in presence of 10 mL of 25% nitric acid to precipitate the silver bromide. The excess of unused silver nitrate was estimated with standard ammonium thiocyanate (0.025 mol dm^{-3}) using ferric alum indicator.

Products Analysis

A mixture of *o*-toluic acid, triethylamine and phenacyl bromide in molar ratio was kept overnight; the solvent was evaporated and the residue in CH_2Cl_2 was washed with 5% $NaHCO_3$, dilute HCl and water. Usual workup was a solid which was characterized by spectral analysis to be:



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