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KINETICS OF REACTION OF TRIETHYLAMMONIUM CARBOXYLATES WITH α-HALOGENOCARBONYL COMPOUNDS IN ORGANIC SOLVENTS

REACTION OF BENZOATES AND PHENOXYACETATES WITH PHENACYL BROMIDE IN ACETONE

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Abstract—The kinetics of the reaction of phenacyl bromide with triethylammonium p-substituted benzoates and phenoxyacetates at 25°, 30° and 35° in acetone suggest a rigid cyclic transition state involving a hydrogen bonded ion-pair as the active nucleophile. The effect of addition of water on the rate constant is rationalized. Regression analysis on single parameter treatment on benzoates shows that the reaction obeys the Hammett equation (ρ value $+0.37$, with $r = 0.993$).

The nature of the complexes formed between amines and carboxylic acids and the extent of complex formation depend on the strength of the acids and bases, the type of the solvent and temperature. The structural and spectral characteristics of these complexes in aprotic solvents have been very extensively studied.[1-7] Almost all of these investigations conclude that the complexes exist as ion-pairs in aprotic solvents. Finer details of the structure of these ion-pairs are decided by the dielectric constant and solvating power of the medium in which they are generated.[2,7] In solvents of low dielectric constants such as carbon tetrachloride, cyclohexane or carbon disulfide triethylamine interacts with carboxylic acids such as acetic acid and benzoic acid by hydrogen bond association with little ionization. But ionization does occur in solvents with intermediate polarity such as chloroform or acetonitrile leading to unusual species which does not show identifiable $\overset{+}{N}H$ absorption. In solvent like dimethyl sulfoxide ionization occurs with relatively little dissociation into free ions.[2] The reactivity of the carboxylate group in any one of the above species is considerably different from metal carboxylates in aqueous or aqueous organic solvents.[8] For example, carboxylic acids undergo esterification with alkyl halides or phenacyl bromides with much facility in the presence of 1,8 - diazobicyclo[5.4.0]undec - 7 - ene (DBU) or triethylamine.[9-11] A survey of literature revealed that these reactions are not much exploited for rate studies.[12,13] In the present paper, we have investigated the kinetics of the reaction of *p*-substituted benzoic acids and phenoxyacetic acids in the presence of triethylamine with phenacyl bromide in acetone with a view to understanding the nature and relative reactivity of the different nucleophiles.

Phenacyl bromide undergoes nucleophilic substitution of bromine atom with a number of nucleophiles readily. The reactivity of the bromine atom is attributed to the electron-withdrawing effect of the carbonyl group.[14] The reactivity of phenacyl bromide towards various nucleophilic species has been analysed by Halvorsen and Songstad[15] and a comparison of the second-order rate constants for the nucleophilic substitution reaction of $PhCOCH_2Br$ with Cl^-, $(NH_2)_2CS$, $NCSe^-$, NCS^-, pyridine, Ph_3P, Me_2S, Ph_3As, Me_2NPh and Et_3N (in MeCN) at 25° revealed that the rate enhancement due to the carbonyl group is not a general effect, but is very dependent upon the nucleophile. Kinetics of the reaction of phenacyl bromides with substituted anilines[16] and the reactions of substituted phenacyl bromides with aniline in methanol[17,18] were investigated and LFER have been applied. Benzoate ion reacts as a good nucleophile in the reaction with phenacyl bromide and the reaction was kinetically analysed for the first time by Rout *et al.*[19] Reaction of phenacyl bromide with *o*-substituted benzoates, 4 - substituted - 1 - naphthoates, 6 - substituted - 2 - naphthoates, 3 - substituted - 2 - naphthoates and phenoxyacetates has been also subjected to substituent effect study by Ananthakrishna Nadar *et al.*[20-23] In all the above studies of reaction of phenacyl bromide with carboxylate ions, the sodium salts were used and the solvent used being acetone water (90:10 or 80:10) mixture. This is the first report of the kinetics of reaction between phenacyl bromide and triethylammonium benzoates or triethylammonium phenoxyacetates in acetone as far as we know.

RESULTS AND DISCUSSION

Triethylammonium benzoates. Previous studies conclude that phenacyl bromide undergoes S_N2 reaction with sodium benzoate in aqueous acetone.[19-23] Kinetics of reaction of triethylammonium benzoate with phenacyl bromide at 30° in acetone and in aqueous acetone was investigated in this paper and the results are presented in Table 1. The magnitude of the decrease is very significant during the initial increase in water composition and becomes less significant as the composition

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Table 1. Effect of water on the rate of reaction of phenacyl bromide with triethylammonium benzoate and phenoxyacetate in acetone

Sl. No.	% of water in aq. acetone	Mole fraction of water	Y values	Benzoate		Phenoxyacetate	
				$k_2 \cdot 10^{3*}$ at 30° C	$\log k_2$	$k_2 \cdot 10^{3*}$ at 30° C	$\log k_2$
1	0	-	-	15.57	-	19.50	-
2	5	0.176	-2.760	8.38	-2.0768	6.20	-2.2076
3	10	0.312	-1.856	6.43	-2.1918	3.77	-2.4237
4	15	0.418	-1.308	4.13	-2.3841	2.08	-2.6828
5	20	0.505	-0.673	3.50	-2.4559	1.52	-2.8182
6	25	0.576	-0.308	3.00	-2.5223	1.10	-2.9594
7	30	0.636	+0.130	2.29	-2.6402	0.91	-3.0402
8	35	0.687	+0.385	1.89	-2.7235	0.69	-3.1610
9	40	0.731	+0.796	1.64	-2.7852	0.56	-3.2496

$^{*}L\ mol^{-1} sec^{-1}$

of water is much increased. The rate constant tends to attain a steady value at high composition of water in the mixture solvent (see Fig. 1). It is important to note that the rate constant has decreased to nearly half by the addition of only 5% water. The presence of small amount of water alters the reactivity of the active species to a greater extent. The rate of reaction of triethylammonium benzoate ($k_2 = 6.43 \times 10^{-3}\ Lmol^{-1} sec^{-1}$) and sodium benzoate ($k_2 = 8.00 \times 10^{-3}\ Lmol^{-1} sec^{-1}$) in 90% acetone are comparable indicating that the attacking nucleophile may be of similar type in both the systems. However, in plain acetone the reactive species may be a different one. Triethylammonium benzoate can exist as an ion-pair and it may have any one of the following structures (for 1:1 complex) in dry acetone: (1) a tight ion-pair with complete proton transfer, (2) a symmetrical carboxylate which is involved in hydrogen bonding with triethylammonium ion,[3] (3) an unsymmetrical structure in which triethylammonium ion is preferentially bonded to one of the oxygen,[3] (4) case (3) in which the solvent molecule also is hydrogen-bonded to the carboxylate. Other than this, the acid can form a 2:1-complex under certain conditions.

We have analysed the solution IR and PMR spectra of triethylammonium bonzoate in acetone to get an idea about the structure of the ion-pair. Triethylamine shows the doublet due to $-CH_2-$ and $-CH_3$ groups at 2800 and 2885 cm^{-1}. Benzoic acid shows the strong broad characteristic peak of -OH between 3400 and 2800 cm^{-1}. The carbonyl peak is masked by strong solvent absorption. In the spectrum of the complex also, the region below 1800 cm^{-1} is not useful for diagnostic purpose and we are not able to recognize the carbonyl absorption or to assign the bands to $\nu a(CO_2^-)$ or $\nu s(CO_2^-)$ or $\nu(CO)$. Nevertheless, the general pattern of the spectrum is similar to that in acetonitrile.[2] There is no recognizable band for $\overset{+}{N}H$ group, there are a number of broad bands between 3500 and 1800 cm^{-1} and the whole curve is underlaid by a strong general absorbance. These observations indicate that there is ion-pair formation when benzoic acid and triethylamine interact in acetone, but the partners of the ion-pair are held by hydrogen bonding as in acetonitrile medium. The precise nature of the hydrogen bonding could not be readily visualized. However, there is no clear evidence for $\overset{+}{N}H$ absorption to indicate that ionization has occurred to yield the species $Et_3\overset{+}{N}H\ C_6H_5COO^-$ (simple ion-pair) which does exist in DMSO.[2]

Triethylamine in acetone-d_6 shows the methyl triplet at 0.92δ and methylene quartet at 2.32δ. In the case of triethylammonium benzoate both these peaks are shifted to 1.19 and 2.92δ, respectively. We have not seen any recognizable absorption in other regions except aromatic absorption. Therefore, it is concluded that benzoic acid and triethylamine are quantitatively converted in acetone to triethylammonium benzoate which appears to exist as a single species as far as NMR spectrum can tell us. The peaks of the complex are shifted to 1.26 and 3.12δ by the addition of 5% D_2O. Further addition of 5% D_2O does not cause much change in NMR peaks (1.26 and 3.16δ). This is in conformity with the kinetic observation that the addition of small amount of water changes the nature of attacking nucleophile.

Benzoic acid undergoes esterification with alkyl halides or phenacyl bromide readily in the presence of DBU or triethylamine.[9-11] This acceleration in activity can be attributed to the coordination of triethylammonium ion with benzoate ion by hydrogen bonding.[9] Hydrogen bond-assisted organic reactions have been realized in recent years.[24] In the presence of fluoride ions, carboxylic acids are good acetoxylating agents.[25] Clark and Miller conclude[24] that it might appear, at first glance, that this is another example of fluoride functioning as a base; however it is more realistic to differentiate this situation from the role of purely a proton acceptor. The fluoride anion may be considered as a source of electrons which

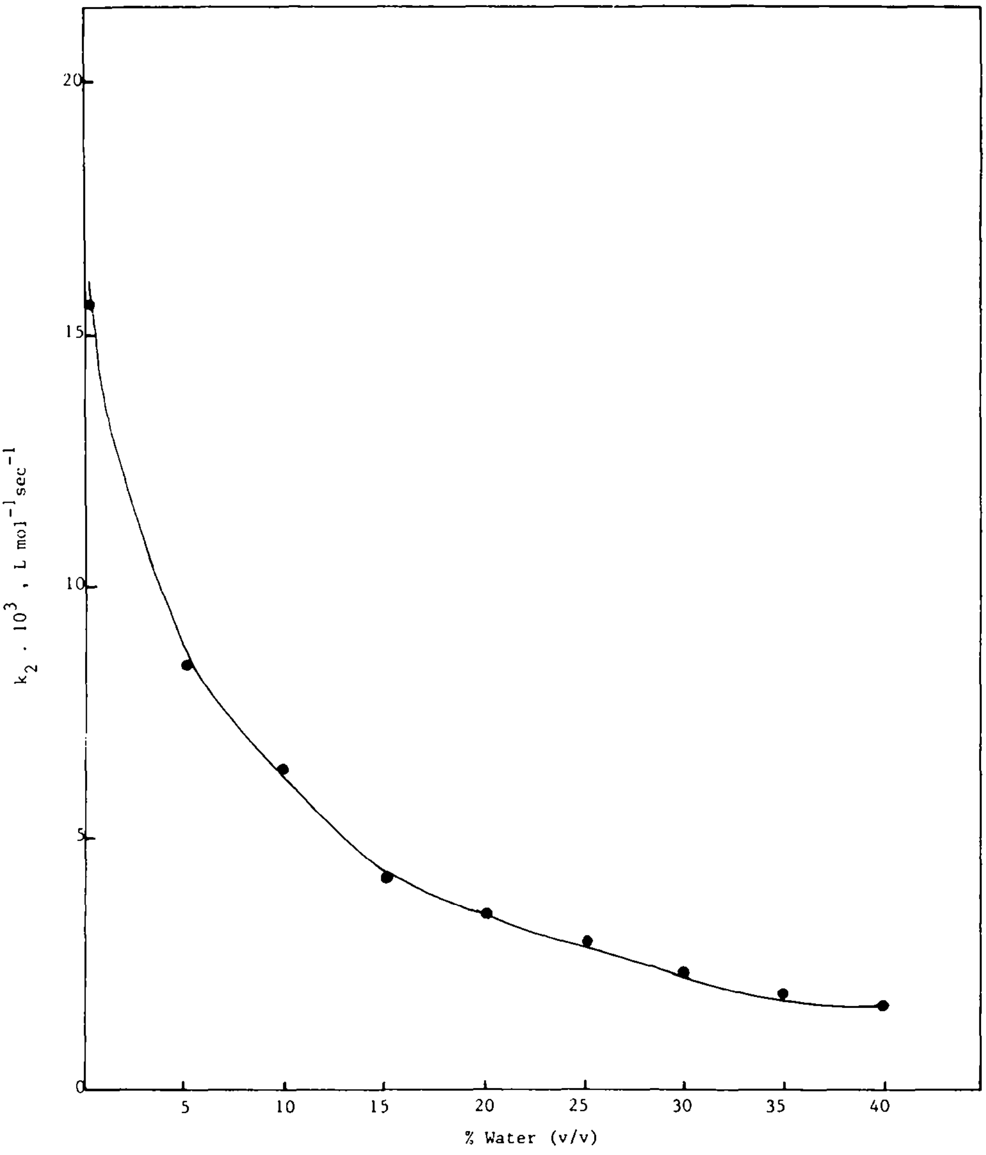


Fig. 1. Plot of k_2 vs % water in acetone.

acts via the H-bond, to transfer negative charge to organic part of the complex, hence generating highly reactive acetoxy anion. Similar situation may exist in the present complex too wherein the triethylammonium group acts as the source of electrons.

The order of reactivities of triethylammonium phenylacetate, benzoate, acetate and phenoxyacetate in acetone is: phenoxyacetate > benzoate > phenylacetate > acetate as given in Table 2. This order is just reverse of the basicity order of the anion, i.e. acetate > phenylacetate > benzoate > phenoxyacetate as determined from the pKa values of the corresponding acids. However, in aqueous acetone reactivity order of sodium carboxylates corresponds to the basicity order.[23] Hence, under the present reaction conditions the active species is different from that in aqueous acetone.

Triethylamine itself can act as a competing nucleophile to react with phenacyl bromide.[10] But in the presence of benzoic acid it exists as the ammonium cation (*vide supra*). Moreover, the product analysis shows that the ketoester is the sole product formed. Even then in all the kinetic runs, care was taken to use exactly equimolar quantities of the acid and triethylamine to avoid the possibility of amine entering into the debromination of phenacyl bromide. In all the kinetic runs the reaction was followed up to approx. 80%.

Free unionized benzoic acid may not enter into reaction with phenacyl bromide. In the absence of triethylamine the reaction of benzoic acid with phenacyl bromide was found to be extremely slow. In one kinetic run, the second-order rate constant was determined for a mixture containing 0.05 M benzoic acid, 0.025 M triethylamine and 0.025 M phenacyl bromide in 100% acetone at 30° and it was found to be 1.37×10^{-2} L mole^{-1} sec^{-1}. Even though 0.05 M of benzoic acid was used only 0.025 M has reacted with triethylamine to form the triethylammonium benzoate which is the active nucleophile. So, while evaluating the rate constant, the rate equation for equal initial concentrations of the reactants had to be used since the initial concentration of

Table 2. The rate constant values for the triethylammonium salts of some organic acids and pK_a values

Acid	$k_2 \cdot 10^2$, L mol^{-1}sec^{-1} 30° C	pK_a
CH_3COOH	0.987	4.76[a]
$C_6H_5CH_2COOH$	1.310	4.31[a]
C_6H_5COOH	1.560	4.20[a]
$C_6H_5OCH_2COOH$	1.950	3.17[b]

[a] Ref. 40. [b] Ref. 41.

triethylammonium benzoate and phenacyl bromide were the same (0.025 M) to get a constant value. The rate constants calculated using second-order rate equation for unequal initial concentrations were found to vary. In another run, a mixture containing 0.05 M benzoic acid, 0.05 M triethylamine and 0.025 M phenacyl bromide (unequal concentrations of triethylammonium bonzoate and phenacyl bromide) in 100% acetone was used. In this case, the rate equation for unequal initial concentrations of the reactants had to be used to evaluate the second-order rate constant (1.54×10^{-2} L mol^{-1} sec^{-1}).

All the above observations indicate that it is the reaction of the ion-pair with phenacyl bromide that was followed in these kinetic runs. In the light of these facts, the mechanism of the reaction is assumed to be very much similar to the one given for the sodium benzoate-phenacyl bromide reaction but the ion-pair is the effective nucleophile in the present case as shown in Scheme 1. During the formation of the transition state, there is a weakening of the binding between the partners of the ion-pair, a weakening of the C–Br bond and formation of a bond between the carboxylate end of the ion-pair and the carbon atom of $-CH_2Br$. Any factor which hinders any one of these phenomena may retard the reaction. However, the precise nature of the transition state can be known only after carefully analysing other kinetic data.

Solvent effect. The magnitude of change in second-order rate constant for triethylammonium benzoate-phenacyl bromide reaction is nearly half when the reaction medium is changed from acetone to 5% aqueous acetone. This considerable decrease may be due to the decomposition of the hydrogen-bonded complex (a reactive species) to a solvent separated ion-pair or to hydrated benzoate ion (less reactive) and triethylammonium ion. Further decrease in rate constant (Table 1) with increasing ionizing power of the solvent (by adding more water) is similar to the trend observed in the reaction of sodium benzoate with phenacyl bromide in aqueous acetone.[26] This can be accounted for on the basis of Hughes-Ingold theory.[27,28] In the S_N2 reaction between benzoate and phenacyl bromide the nucleophile is more polar than the transition state. Therefore the reactant is more and more stabilized with increasing ionizing power of the medium.

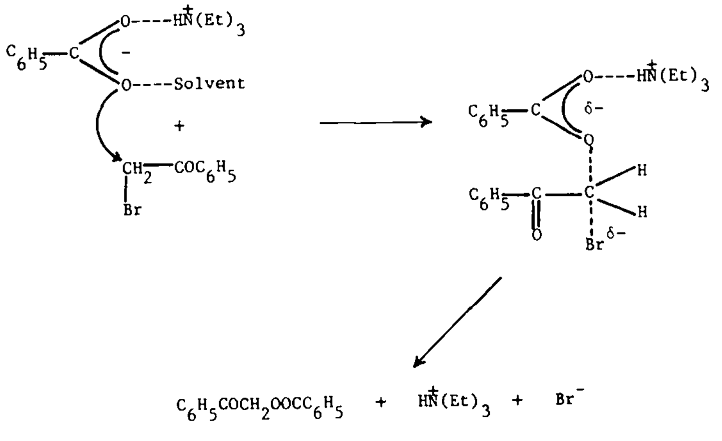
The log k_2 values are also correlated with Grunwald–Winstein Y values to study the solvent effect on the system.[29] To apply Grunwald–Winstein eqn (1) the Y values of the solvent pairs are taken from the literature.[30] Some Y values are obtained by

$$\log k = \log k^{c} + mY \qquad (1)$$

interpolation. The log k_2 values and the Y values used for computation are given in Table 1. The eight data points in Table 1 have been fitted to eqn (1) by least squares analysis to yield the regression equation (2) with a simple correlation coefficient,

$$\log k_2 = -2.616 - 0.205\,Y \qquad (2)$$

$r = 0.993$ and the standard deviation of the estimate, $s = 0.03$. Hence, there is a good relationship between the



Scheme 1.

rate constant values and Y values of the solvent mixtures. The low value of m(0.205) suggests that the bond breaking and bond formation have proceeded to the same extent which is characteristic of S_N2 reactions.

Substituent effects and thermodynamic parameters. The rate constants for *p*-substituted benzoic acids have been determined at 25°, 30° and 35° in 100% acetone and are presented in Table 3. A comparison of the rate constants in Table 3 shows that electron-releasing substituents like -OH, $-NH_2$, $-OCH_3$, $-CH_3$ and -NHCOPh act as retarders while halogens and electron-withdrawing substituent like $-NO_2$, act as accelerators for the reaction. The 4-fluorobenzoic acid behaves very much similar to the unsubstituted compound. This may be due to the cancellation of the −I effect of fluorine by an almost equivalent +M effect. However, the reactivity order shown in Table 3 is different from the expected order based on the kinetic studies on the reaction of sodium benzoates.[19–22] This can be rationalized only when the thermodynamic parameters are analysed carefully.

The activation parameters were evaluated in the usual way and presented in Table 3. An analysis of the entropy values given in Table 3 leads to interesting conclusions. In general, this series is manifested by high negative entropy of activation. The solvent effect indicates that the transition state is less polar compared to the reactants. The decrease in entropy may not, therefore, arise from solvation of the activated complex. A greater crowding in the transition state is mainly responsible for a higher rigid transition state leading to considerable decrease in entropy. The $\Delta S^{\neq}$ values for the reactions of sodium benzoate, sodium-2-naphthoate, sodium-1-naphthoate and phenoxyacetate with phenacyl bromide in aqueous acetone are compared with that of the present

Table 3. Second-order rate constants and activation parameters for the reaction of phenacyl bromide with *para*-substituted benzoic acids in the presence of triethylamine in acetone

Sl. No.	Substituent	$k_2 \cdot 10^2$, L mol^{-1}sec^{-1}*			$\Delta H^{\#}$ k cal mol^{-1}	$-\Delta S^{\#}$ e.u.
		25° C	30° C	35° C		
1	4-NH_2	0.604	0.806	1.05	9.2	37.8
2	4-OH	0.600	0.782	1.00	8.8	39.2
3	4-NHCOPh	0.945	1.29	1.73	10.5	32.8
4	4-OCH_3	0.994	1.47	1.73	9.5	35.9
5	4-CH_3	1.14	1.47	1.89	8.6	38.5
6	4-H	1.18	1.56	2.22	11.1	30.2
7	4-F	1.15	1.55	2.22	11.4	29.2
8	4-Cl	1.35	1.71	2.82	12.9	23.9
9	4-Br	1.28	1.68	2.57	12.2	26.4
10	4-I	1.28	1.64	2.46	11.3	29.5
11	4-NO_2	1.21	1.65	2.36	11.7	28.2

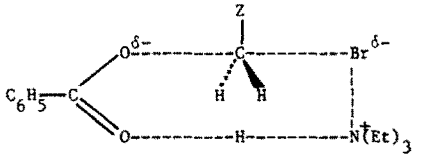
*k_2 is reproducible within ±3%.

Table 4. Entropy of activation for the reaction some carboxylates with phenacyl bromide

Sl.No.	Nucleophile	$-\Delta S^{\#}$, e.u.	References
1	$C_6H_5COO^- \; H\overset{+}{N}(Et)_3{}^a$	30.3	Present work
2	$C_6H_5COO^- \; Na^{+\,b}$	3.8	20
3	$1\text{-}C_{10}H_7COO^- \; Na^{+\,b}$	21.5	21
4	$2\text{-}C_{10}H_7COO^- \; Na^{+\,b}$	1.4	22
5	$C_6H_5OCH_2COO^- \; H\overset{+}{N}(Et)_3{}^a$	38.8	Present work
6	$C_6H_5OCH_2COO^- \; Na^{+\,c}$	14.0	23

[a] Acetone. [b] Aqueous acetone 90%. [c] Aqueous acetone 80%.

reaction in Table 4. It is quite obvious that for the present system, the entropy decrease is very significant compared to others. On this basis, a cyclic transition state of the following type **1** has been visualized for the reaction between triethylammonium benzoate and phenacyl bromide. In the transition state it is shown that the methylene carbon of phenacyl bromide is subjected to S_N2 reaction by the oxygen of the hydrogen-bonded benzoate and the bromine 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 $\Delta S^{\neq}$ becomes more negative.



Z = C_6H_5CO-

1

Isokinetic relationship. A linear relationship between the entropy and enthalpy of activation of benzoates has been found. This proves that the same mechanism operates in this series as it is required in order to correctly apply LFER. In the isokinetic plot of $\Delta H^{\neq}$ vs $\Delta S^{\neq}$ the eleven data points in Table 3 were subjected to least squares analysis and the correlation coefficient, r, was found to be 0.997 with $s = 0.11$. The least squares values for the intercept, $\Delta H_0^{\neq}$ and the slope, β (isokinetic temperature) were obtained as 19.5 kcal mol^{-1} and 276 K, respectively. The reaction runs were carried out either at 25°, 30° or 35° and so always the reaction temperatures are above the isokinetic temperature. This explains, why the order of reactivities of the substituents observed is contrary to our expectation.[31,32] An electron-withdrawing substituent from p-position should make the ion-pair, a weaker nucleophile and thus should retard the rate. Similarly an electron-releasing substituent must increase the nucleophilicity of the ion-pair and thus should accelerate. The observations that the electron-releasing substituents, $-CH_3$, $-OCH_3$, $-NH_2$, -OH, etc. were found to retard the rate while the halogens and the electron-withdrawing substituents like $-NO_2$ were found to accelerate the reaction rate are accounted on the basis that the reaction temperatures are above the isokinetic temperature. We derive more confidence for this conclusion from the results of the kinetic study on the reaction of phenacyl bromide with phenoxyacetic acids in the presence of triethylamine where the order of the reactivities is as expected since the reaction temperature is below the isokinetic temperature (see Table 5) in every run.

Linear free energy relationships with Hammett substituent parameters. The plot of $\log k_2/k_2^0$ of p-substituted benzoates at 35° vs σ has been found to be linear (Fig. 2). For -OH and $-NH_2$ groups the σ_p^+ values and for all the other groups the Hammett σ values are used in the correlation[33-35] since in the case of -OH and $-NH_2$ substituted benzoic acids conjugative interaction between the substituent and the carboxylate group is possible. Except the $-NH_2$ and $-NO_2$ groups all the other groups show linear relationship.

We correlated the logarithms of the rate constants at 35° for the reaction of substituted benzoic acids with phenacyl bromide by the following Hammett equation,

$$\log k_2 = \log k_2^0 + \rho\sigma. \tag{3}$$

The data from Table 3 except those of $-NH_2$ and $-NO_2$ have been fitted to the equation by the least squares analysis to yield the following result:

$$\log k_2 = -1.665 + 0.367\sigma. \tag{4}$$

The correlation coefficient for a set of ten data points fitted into eqn (4) is found to be 0.993. The reaction constant, ρ, calculated by the linear regression analysis is

Table 5. Rate constants and activation parameters for the reaction of phenacyl bromide with phenoxyacetic acids in the presence of triethylamine in acetone

Sl. No.	Substituent	$k_2 \cdot 10^2$, L mol^{-1}sec^{-1}* 30° C	35° C	40° C	$\Delta H^{\#}$ k cal mol^{-1}	$-\Delta S^{\#}$ e.u.
1	H	1.95	2.30	3.14	8.4	38.8
2	4-CH_3	1.95	2.53	3.14	8.2	39.1
3	4-NO_2	1.49	2.04	2.77	11.0	30.3
4	4-Cl	1.57	2.17	2.94	11.2	29.8
5	4-Br	-	2.27	3.13	11.7	28.1
6	4-I	1.43	2.26	2.84	12.3	26.3
7	2-CH_3	1.57	2.00	2.77	10.1	33.6
8	2-NO_2	1.48	1.82	2.38	8.5	39.1
9	2-Cl	1.60	2.22	2.74	9.5	35.3

*k_2 is reproducible within ±3%.

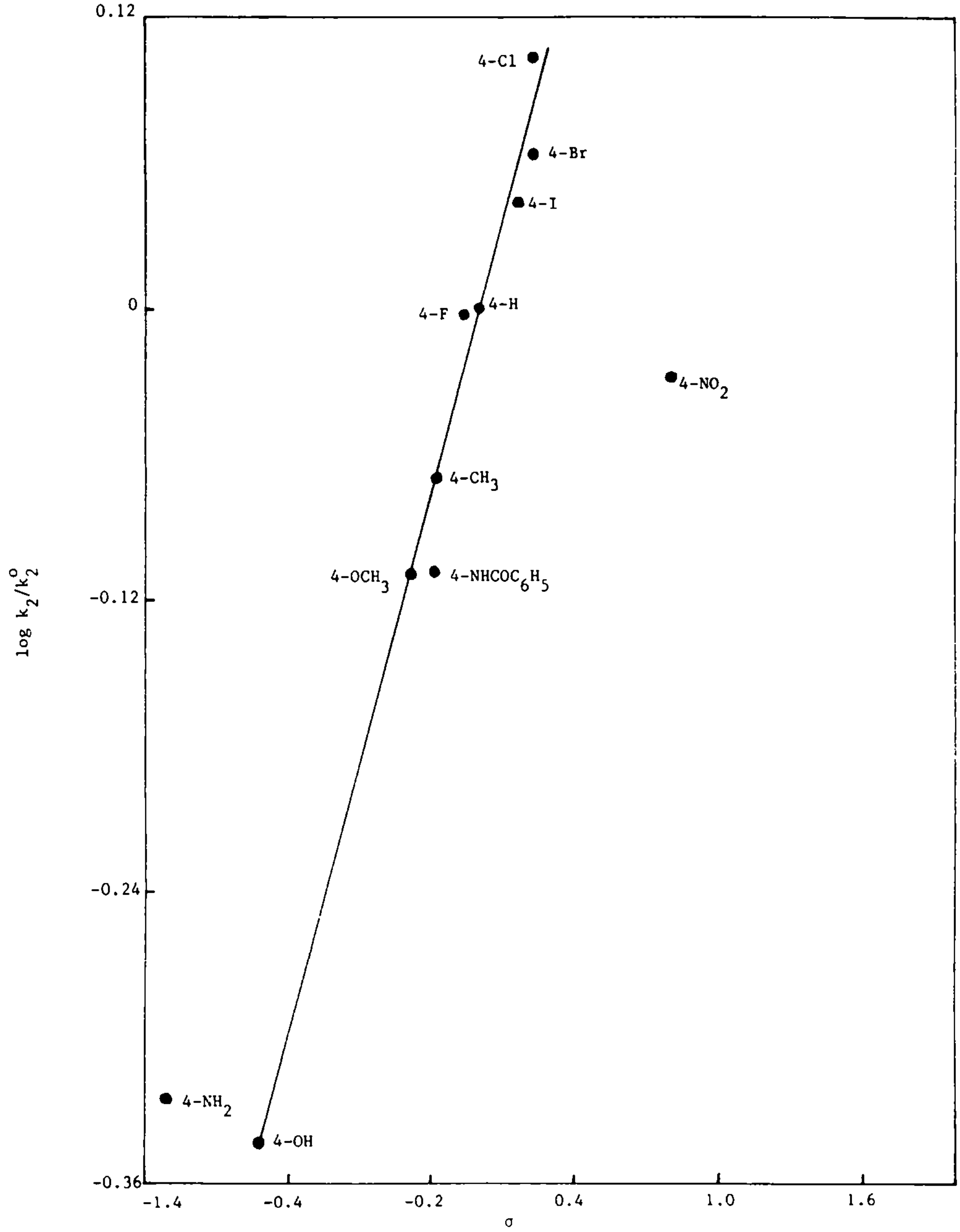


Fig. 2. Log k_2/k_2^0 vs σ.

+0.367. The magnitude of ρ indicates that this series shows less sensitivity to substituent changes than the ionization of substituted benzoic acids.

The values of $\log k_2$ for the various substituted benzoic acids in this reaction series have been evaluated using eqn (4) and a plot of $\log k_{2(obs)}$ vs $\log k_{2(cal)}$ gives points most of which fall in the 45° line indicating that the estimation and observation are in good agreement.

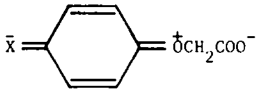
In the case of *para*-aminobenzoic acid, the second-order rate constant calculated using enhanced σ_p^+ value in eqn (4) is $0.70 \times 10^{-2}\,\mathrm{L\,mol^{-1}\,sec^{-1}}$ while the observed value is $1.05 \times 10^{-2}\,\mathrm{L\,mol^{-1}\,sec^{-1}}$ at 35°. The higher experimental value indicates that in addition to the $-COO^-$ group, the $-NH_2$ group may also be entering into reaction since the amino function is also a potential nucleophile in the debromination of phenacyl bromide. This may be the reason for the deviation of the point for the *p*-aminobenzoic acid from the correlation line. When the amino compound is also included in the linear regression analysis, the correlation becomes poor with $r = 0.97$. The anomalous behaviour of *p*-nitrobenzoic acid could not readily reationalized.

Triethylammonium phenoxyacetates. The effect of added water on the rate of the reaction of triethylammonium phenoxyacetate is analogous to benzoate (Table 1). The initial addition of 5% water causes more notable decrease (19.5–$6.2 \times 10^{-3}\,\mathrm{L\,mol^{-1}\,sec^{-1}}$) in the rate than in the case of benzoate. Water molecules may coordinate with phenoxyacetate efficiently compared to benzoate due to the presence of an additional oxygen atom in the former and dissociate the hydrogen-bonded complex effectively. This factor is responsible for the notable retardation (3 times) of the reaction rate. The log k_2 values and Grunwald–Winstein Y values are fitted into eqn (1) to get

$$\log k_2 = -3.027 - 0.299Y \qquad \begin{matrix} r = 0.99 \\ s = 0.03. \end{matrix}$$

The low value of m(0.299) is characteristic of S_N2 reaction.

A comparison of the rate constants given in Table 5 indicates that electron-donating methyl substituent has no appreciable effect. Electron-withdrawing nitro group retards the rate by inductive and mesomeric mechanisms. The *p*-oxygen group readily conjugates with nitro group and develops a positive charge on oxygen. Along the side chain, after oxygen the polar effect is transmitted inductively. The halogen substituents also retard the rate of the reaction indicating that they act as electron-acceptors. Halogens other than fluorine can act as electron-acceptors utilizing their d-orbitals when suitable electron-donating substituent is present in the para position.[36] In the present case, the side chain, $-O-CH_2COO^-$ is comparable to $-OCH_3$ group and so one can visualize the contribution of a canonical structure of type **2**. Among the *p*-substituents the reactivity order is $p\text{-Me} \approx H > p\text{-Br} > p\text{-I} > p\text{-Cl} > p\text{-NO}_2$. All the ortho substituents studied decrease the rate compared to the unsubstituted. Hence, the steric and polar effects may play an important part in this situation. The reactivity order is $H > o\text{-Cl} > o\text{-Me} > o\text{-NO}_2$. In the case of o-NO_2 substituent both -I and -M effects reinforce one another and decrease the rate considerably.



2   X = Cl, Br, I or NO_2

The thermodynamic parameters were evaluated in the usual way. Electron-donating substituents decrease the energy of activation and electron-withdrawing substituents increase the energy of activation in the *p*-series (Table 5). Similar is the trend with enthalpy of activation. This reaction series also is characterized by high negative entropy of activation (Table 5). This is due to a greater crowding in the transition state leading to a rigid cyclic transition state of the type **1**.

A linear relationship exists between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the *p*-series. In the equation $\Delta H^{\neq} = \Delta H_0^{\neq} + \Delta S^{\neq}$, $\Delta H_0^{\neq}$ has the value 20.5 k cal mol^{-1} and the slope $\beta = 312.6$ K (isokinetic temperature). This linear relationship shows that the same mechanism operates in the whole series. The reaction temperatures are nearer to the isokinetic temperature and so a low magntiude of the substituent effect can be anticipated.[31,32] The logarithms of rate constants of phenoxyacetates and Hammett *p*-substituent constants are correlated by simple regression to yield the result

$$\log k_2 = -1.628 - 0.0888\sigma \tag{8}$$

with r = 0.93 and s = 0.15. Since the magnitude of ρ is very low this reaction series is less susceptible to substituent effects. In the case of *ortho*-substituted compounds studied the log k_2/k_{2Me} values do not correlate with σ_o^*, the Taft's polar substituent constant for *ortho* compounds, but there is a linear relationship between log k_2/k_{2Me} values and the steric substituent constant E_s.

EXPERIMENTAL

Materials. Technical grade benzoic acid, *p*-hydroxybenzoic, *p*-aminobenzoic, *p*-nitrobenzoic and *p*-chlorobenzoic acids were recrystallized from water until their m.ps remained constant after subsequent crystallization and agreed with the literature values. *p*-Anisic, *p*-toluic, *p*-bromobenzoic, *p*-fluorobenzoic, and phenoxyacetic acids[37] were prepared by the best available procedure. Phenacyl bromide was prepared by the bromination of acetophenone following the procedure of Cowper and Davidson.[38]

Rate measurements. The reactions were carried out in acetone (BDH AnalaR used as such). The thermostated soln (∓0.01°) of phenacyl bromide (25 mL, 0.05 M) and 25 mL of 0.05 M soln of carboxylic acid containing triethylamine (0.05 M) in acetone were mixed. The course of the reaction was followed by pipetting out 5 mL of aliquots of the reaction mixture at different intervals of time, adding it to 10 mL of (0.025 M) silver nitrate soln in the presence of 10 mL of 25% nitric acid and titrating against standard ammonium thiocyanate soln (0.025 M) using ferric alum as the indicator. Since equimolar quantities of the reactants were employed the second order rate constant, k_2, was evaluated using the equation $k_2 = 1/t\ X/a(a - X)$. It was observed by duplication of runs that the rate constant could be reproduced with an accuracy of ±3%.

Product analysis. Fifty mL of 0.05 M soln of phenacyl bromide (0.497 g) in dry acetone was mixed with 5 mL of 0.05 M soln of triethylammonium benzoate (benzoic acid 0.305 g and triethylamine 0.252 g) and kept at 25° for 20 hr. Acetone was stripped off in a flash evaporator. The residue was dissolved in CH_2Cl_2 (50 mL), washed with water, sodium bicarbonate (5%) and finally with water and dried over anhydrous sodium sulfate. Removal of solvent afforded the product phenacyl benzoate in 92% isolated yield (0.55 g) which was found to be pure by TLC; m.p. 118–120° (lit.[39] 119–121°). NMR 5.60δ (s, 2H); two multiplets 7.42–7.72δ and 7.90–8.24δ (together 10 H); IR(KBr) 1720 cm^{-1} (ester C=O), 1695 cm^{-1} (ketone C=O) and 1280 cm^{-1} (C–O).

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