The R_4NI salts (M/s Distillation Products Industries, USA) were purified in the usual manner[11]. Solutions were prepared on molal basis and the density was determined with a dilatometer of about 40 ml capacity, the stem of which was graduated in 0·01 ml so that volume could be read with ease up to 0·003 ml within an error not exceeding 0·002 ml with a magnifying glass. Rest of the experimental procedure was the same as given in earlier communications from this laboratory. From the density data at 40°, apparent molal volume was obtained in the usual manner. Only Me_4NI, Et_4NI, Pr_4NI and Bu_4NI could be studied since the higher homologues have little solubility in this solvent medium.

The linear plots of ϕ_v versus $\sqrt{C}$ (Fig. 1) indicate the applicability of the Mason's equation, $\phi_v = \phi_0 + S_v\sqrt{C}$, to these solutions within the concentration range studied. The slope of the curves for Me_4NI and Et_4NI is positive in all the five mixtures. However, for Pr_4NI, it is negative in mixtures containing 9·47 and 19·84% methanol and becomes positive at higher concentrations of methanol. The slope is negative for Bu_4NI in mixtures containing 9·47, 19·84 and 34·48% methanol and then becomes positive. Comparing the results obtained in the present study with those in water-dioxane mixtures[1], it appears that change over of the negative slope to a positive one, occurs at $\epsilon \simeq 60$ for Bu_4NI in both water-dioxane and water-methanol mixtures and for Pr_4NI, it appears at $\epsilon \simeq 63$-64 in water-methanol and at $\epsilon \simeq 69$ in water-dioxane mixture. In view of the approximate nature of these estimates, it is justified to assume that change over from a negative to a positive slope for a given salt occurs around the same approximate value of the dielectric constant. The change in the nature of the molecular species (dioxane is non-polar and without hydrogen bonding whereas methanol is polar with hydrogen bond interaction) does not seem to have any appreciable effect. It is only the dielectric constant of the medium which matters. With the limited data in a few solvent systems, it is not possible to make any generalization.

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Kinetics of Reaction Between o-Substituted Benzoate Ions & Phenacyl Bromide

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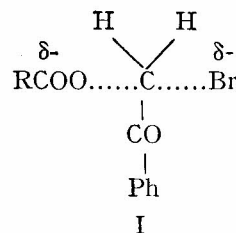V.H.N.S.N. College, Virudhunagar 626002

The rate of reaction of phenacyl bromide with various o-substituted benzoate ions has been measured in 90% (v/v) acetone-water mixture at 30°, 35° and 40°. Arrhenius parameters as well as the enthalpies and the entropies of activation have been evaluated. The reaction does not obey the Brönsted relationship. The isokinetic temperature unexpectedly is found to be well below the ambient temperature. Though the behaviour of o-substituents is correlated with their polar effects by the Taft equation, it appears that some substituents behave quite unexpectedly. This may be due to the fact that the values of k are all obtained above the isokinetic temperature. The polar substituent constants, σ_0^*, for SCH_3 and SO_2CH_3 groups are evaluated by interpolation in the Taft plot. Variation in $\Delta S^{\ddagger}$ has been explained in terms of the bulk effect of the groups.

KINETICS of reaction of m-, p- and a few o-substituted benzoate ions with phenacyl bromide have been recently reported by Rout and coworkers[1]. But a systematic study on the influence of o-substituents has not so far been made in this reaction and thus a study to understand the effect of o-substituents in this reaction appeared necessary.

The kinetics of the reaction between a number of o-substituted benzoate ions and phenacyl bromide are presented in this paper.

The kinetic results are summarized in Table 1. Based on the results obtained by Ananthakrishna Nadar and Gnanasekaran[2] in the reaction of 6-substituted ω-bromo-2-acetonaphthones with benzoate ion, we have proposed transition state (I) in this reaction.

$$\begin{array}{ccc} & H \quad\quad H & \\ \delta- & \diagdown\;/ & \delta- \\ RCOO\ldots\ldots & C & \ldots\ldots Br \\ & | & \\ & CO & \\ & | & \\ & Ph & \end{array}$$

I

This shows that the attack is at a point remote from o-substituents in the benzene ring. This means that the primary steric effect[3] is absent in this reaction and its contribution to the total effect of the substituents is also absent. But the secondary steric effect[4] of the o-substituents may be expected to make contribution. Presumably conjugation between ring and carboxy side-chain will stabilize the ester product and some sign of this might appear in the transition state and be subject to steric inhibition which will lead to retardation. Therefore, the major effects of
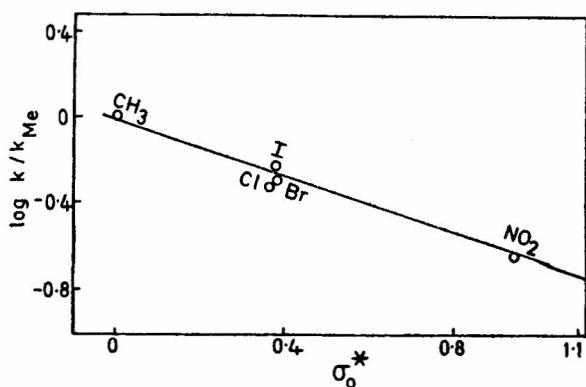
Fig. 1 — Taft plot at 40°

o-substituents that are expected to influence the rate may be their polar and secondary steric effects.

A plot of log k/k_{Me} at 40° against σ_0^* values is linear (Fig. 1) giving a value of -0.63 for the polar reaction constant (ρ^*) with correlation coefficient $r = 0.970$. This indicates that the reaction conforms to the Taft linear polar energy relationship[5]. The SCH_3 and SO_2CH_3 groups are assigned σ_0^* values of 0.18 and 0.89 respectively by interpolation in the above plot.

It is difficult to say with certainty that the above mentioned two effects alone operate in this series. A pattern in which the o-chloro compound reacting almost close to the parent compound and the o-methyl compound reacting much faster than the parent compound cannot possibly fit with this. The Taft plot is effectively a three point correlation and its validity can also mean that all the substituents in question show approximately the same steric effect as methyl, and this is a steric acceleration for the replacement of H by any other group. Indeed, it is difficult to imagine that this reaction is subject to steric acceleration. That the substituents do not exhibit their normal steric effect is known from the very poor correlation in the plot of log k/k_{Me} against Es, the steric parameters of o-substituents. Therefore, it is a situation in which the substituents (at least some) behave quite unexpectedly and this prevents us from making a more quantitative approach to the problem.

The cause for this unusual behaviour may possibly lie in the isokinetic temperature, β. As explained by Exner[6,7], the isokinetic relationship in this reaction has been examined through a plot of log k_1 versus log k_2 where k_1 refers to the rate constant at temperature T_1 and k_2 to the constant at

temperature T_2, T_1 being greater than T_2. If we take $T_1 = 313°K$ and $T_2 = 303°K$ in this series, a plot of log k_1 versus log k_2 is fairly rectilinear with a slope $b = 1.183$ (by least squares). This gives $\beta = 258°K$, which is below the lowest experimental temperature. This may be due to the negative ρ^* value and the negative relative enthalpies of activation ($\Delta\Delta H^{\ddagger}$) observed for many compounds[8]. When the rate constants are obtained above the isokinetic temperature, their pattern for the different substituents is difficult to interpret and it would be quite different at temperatures well below the isokinetic temperature[9].

The plot between rates and pK values of the conjugate acids is not linear indicating the failure of Brönsted relationship[10] in this reaction. This failure may be due to different effects of o-substituents separately influencing rate and acidity.

Substituent effects on $\Delta S^{\ddagger}$ — Though the pattern of log k values poses problem to attribute it to any definite effect, the variation in $\Delta S^{\ddagger}$ can be best explained by the bulk effect of the substituents. A bulky substituent near the reaction centre will reduce the number of energy levels available to the transition state relative to those in the initial state and this renders $\Delta S^{\ddagger}$ more negative[11]. The data in Table 1 reveal that the $\Delta S^{\ddagger}$ values for all the o-substituted compounds are lower than that for the unsubstituted compound. As the size of the group increases $\Delta S^{\ddagger}$ becomes more negative. The methyl and the bromo substituents have approximately the same van der Waals radius[12] and have nearly the same bulk. The $\Delta S^{\ddagger}$ value for o-bromo compound is found to be slightly more negative as compared to that for o-methyl compound. This may be due to the increase in effective radius of the reaction site as a result of increased solvation caused by the negative end of the carbon-bromine dipole thereby increasing the bulk effect of bromine. Even though chlorine has same van der Waals radius[13] as methyl, it exhibits unexpectedly lesser bulk effect than Me.

Benzoic acid and o-toluic acid were commercially available and were recrystallized from gla. acetic acid. o-Iodobenzoic acid was prepared from anthranilic acid and purified by repeated sublimation under reduced pressure and crystallization from water. o-Chloro, o-bromo and o-nitrobenzoic acids were prepared by the oxidation of the corresponding toluenes. o-Methylsulphonylbenzoic acid was prepared by hydrogen peroxide oxidation of o-methylmercaptobenzoic acid. All the acids had

TABLE 1 — RATES OF REACTION BETWEEN o-SUBSTITUTED BENZOATE IONS AND PHENACYL BROMIDE

o-Substituent	$10^3 \times k$ (litre mole^{-1} sec^{-1})			Ea kcal mole^{-1}	$\Delta H^{\ddagger}$ kcal mole^{-1}	$\Delta S^{\ddagger}$ e.u.	log PZ
	30°	35°	40°				
H	8.5	12.6	23.7	20.0	19.4	3.8	12.4
Cl	8.0	11.5	22.3	20.0	19.3	4.4	12.3
Br	8.4	12.4	22.6	18.7	18.1	8.4	11.4
I	10.8	18.6	27.5	17.3	16.7	12.3	10.5
CH_3	16.5	30.2	45.0	18.7	18.1	6.9	11.7
SCH_3	12.1	22.3	33.1	19.2	18.6	5.8	12.0
SO_2CH_3	5.2	10.7	11.0	14.6	14.0	22.7	8.3
NO_2	4.6	7.1	10.4	15.8	15.2	19.2	9.0

m.ps. identical with, or very close to those recorded in the literature.

Analar acetone was purified by the method of Sachs[14] and diluted with triply distilled water. Phenacyl bromide and sodium salts of the acids were prepared by well-known procedures.

Rate measurement — The solvent used was acetone-water 90% (v/v). The temperature was controlled to within ± 0·05°. The kinetic procedure was as reported in literature[15]. It was convenient to use low concentrations (0·02M) of both the reactants for following the kinetics satisfactorily. The equation used to calculate the rate constants k (litre mole^{-1} sec^{-1}) was the second order rate expression with the reactants present in equal concentration. The rate constants were reproducible within ±2%.

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Kinetics & Mechanism of Alkaline Hydrolysis of Salicylamide

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The kinetics of the hydrolysis of salicylamide has been studied under strongly alkaline medium. The observed pseudo first-order rate constants vary according to the empirical equation $\dfrac{1}{k_{obs}} = B_1 + \dfrac{B_2}{[OH^-]}$ at lower [OH⁻] (0·7-1·9M) and an independent rate is observed at higher [OH⁻] (1·9-3·0M). On the basis of these results, a plausible mechanism has been suggested. The existence of dianionic reaction intermediate is ruled out.

KINETICS of hydrolysis of salicylamide in acidic and alkaline media has been investigated by a number of workers[1-3]. In view of the postulate regarding the evidence of additional dianionic intermediate[4-9] in acyl transfer reactions, it was considered worth while to investigate the kinetics of hydrolysis of salicylamide in strongly alkaline medium to ascertain the existence of additional dianionic intermediate.

Salicylamide (E. Merck) was used as such. Its freshly prepared solution in 0·5M NaOH was used for each set as no appreciable reaction occurred under these conditions at room temperature. Other chemicals used were of reagent grade. The reaction was followed by estimating ammonia evolved spectrophotometrically by Nesselerization method[10-15].

The effect of [salicylamide] on reaction rate was studied at 95° in 3·0M NaOH and the values of rate constant $k_{obs} \times 10^3$ (min^{-1}) were found to be 4·49, 3·70, 3·98, 3·35 and 3·62 at [salicylamide] = 0·008, 0·007, 0·006, 0·005 and 0·004M respectively. Studies were also carried out at different temperatures and activation parameters were evaluated using Eyring and Arrhenius equations. The values are: $E_a = 14·9 \pm 0·6$ kcal mole^{-1}, $\Delta S^{\ddagger} = -39·7 \pm 1·8$ e.u.; $\Delta H^{\ddagger} = 14·2 \pm 0·6$ kcal mole^{-1}. The rate increased slowly with the increase in ionic strength.

The rate dependence on [OH⁻] was studied at 95° in NaOH solutions of concentration ranging from 0·7 to 3·0M keeping ionic strength constant at 3 by adding NaNO₃ solution. It was found that the rate increased at [OH⁻] = 0·7 to 1·9M and was independent of [OH⁻] at higher concentrations (−1·9 to 3·0M). In the lower range the rate constants were found to follow the empirical Eqn (1) (Fig. 1).

$$\frac{1}{k_{obs}} = B_1 + \frac{B_2}{[OH^-]} \qquad \ldots(1)$$

The mechanism consistent with the observed results may be represented by scheme 1.

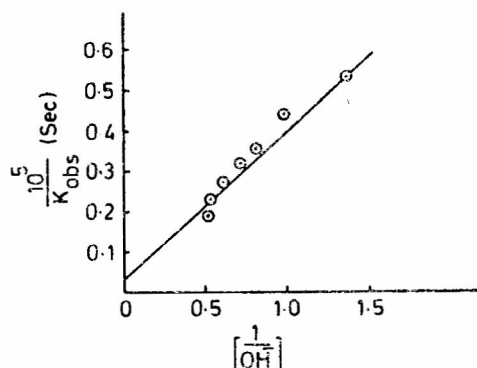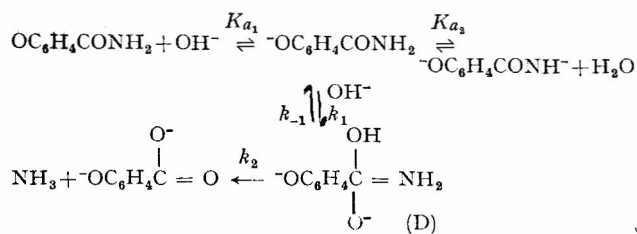As pKa value of salicylamide is of the order ~7-8, it will remain in ionized form in highly alka-

Fig. 1 — Plot of $\dfrac{1}{K_{obs}}$ vs $\dfrac{1}{[OH^-]}$

The line is drawn from the calculated values of rate constants from equation (3). The points are the observed values of rate constants at various [OH⁻].

$$OC_6H_4CONH_2 + OH^- \overset{Ka_1}{\rightleftharpoons} {}^-OC_6H_4CONH_2 \overset{Ka_2}{\rightleftharpoons}$$
$${}^-OC_6H_4CONH^- + H_2O$$

$$NH_3 + {}^-OC_6H_4\overset{\overset{\displaystyle O^-}{|}}{C} = O \xleftarrow{k_2} {}^-OC_6H_4\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle O^-}{|}}{C}} = NH_2 \quad (D)$$

Scheme 1

line medium. The observed pH-rate profile indicates that the contribution to the rate through the dianionic tetrahedral addition intermediate is almost negligible probably due to the presence of ionized phenolic group. The steady state treatment to the reactive tetrahedral addition intermediate (D) leads to the kinetic Eqn (2).

$$K_{obs} = \frac{k_1 k_2 \dfrac{Ka_1}{K_w}[OH^-]^2}{(k_{-1}+k_2)\left(1 + \dfrac{Ka_1}{K_w}[OH^-] + \dfrac{Ka_1}{K_w}\cdot\dfrac{Ka_2}{K_w}[OH^-]^2\right)} \quad ...(2)$$

The Eqn (2) is further reduced to the Eqn (3) by applying the condition that

$$1 < \left(\frac{Ka_1}{K_w}[OH^-] + \frac{Ka_1}{K_w}\cdot\frac{Ka_2}{K_w}[OH^-]^2\right)$$

which is satisfactorily acceptable as Ka_1 is of the order $\sim 10^{-8}$.

$$K_{obs} = \frac{k_1 k_2 [OH^-]}{(k_{-1}+k_2)\left(1 + \dfrac{Ka_2}{K_w}[OH^-]\right)} \quad ...(3)$$

Eqn (3) is similar to the best fitted empirical Eqn (1) with

$$B_1 = \frac{(k_{-1}+k_2)}{k_1 k_2}\cdot\frac{Ka_2}{K_w} \text{ and } B_2 = \frac{(k_{-1}+k_2)}{k_1 k_2}$$

At relatively higher $[OH^-]$ the condition that $1 < \dfrac{Ka_2}{K_w}[OH^-]$ is found to be kinetically more pronounced and hence Eqn (3) is further reduced to Eqn (4),

$$K_{obs} = \frac{k_1 k_2}{(k_{-1}+k_2)Ka_2/K_w} \quad ...(4)$$

which shows that the rate is independent of $[OH^-]$.

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Kinetics of Oxidation of Cinnamyl Alcohol with Chloramine-T in Hydrochloric Acid Medium

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The kinetics of oxidation of cinnamyl alcohol by chloramine-T in the presence of hydrochloric acid (0·1-0·3M) has been studied at 0°. The reaction shows first order dependence on [chloramine-T], second order in [H$^+$] and is independent of [substrate]. The energy and entropy of activation of the reaction have been found to be 57·2 KJ mole^{-1} and −75·01 JK^{-1} respectively. The Arrhenius factor is 1·203 × 10^9 sec^{-1}. Ionic strength and presence of p-toluenesulphonamide have very little influence on the rate of reaction. The proposed mechanism assumes a stepwise addition of two protons to release the precursor chlorinium ion, which on hydrolysis yields H$_2$OCl$^+$. The latter attacks the substrate in a fast step to form the reaction products, cinnamic aldehyde and p-toluenesulphonamide.

IT was earlier[1] noticed that cinnamyl alcohol in 50% aq. ethanol (v/v) underwent ready oxidation by chloramine-T (CAT) in the presence of HCl (0·1 to 0·3M). The results of kinetic studies of this reaction are reported in this note. Since the reaction is fairly rapid at room temperature (25°), the kinetic runs were made at 0°.

Chloramine-T (E. Merck) was purified by the method of Morris et al.[2] and its aqueous solution standardized by the iodometric method. Stock solutions of cinnamyl alcohol (Naarden, b.p. 256·6°) were prepared in 50% aq. ethanol (v/v). A concentrated solution of sodium perchlorate was used to keep the ionic strength constant. All other chemicals used were of analytical reagent grade. The experimental procedure has been described earlier[1].

Stoichiometry—Reaction mixtures containing excess CAT over cinnamyl alcohol in the presence of HCl (overall concentration, 0·5 to 1·0M) were kept at room temperature (25°) for 24 hr. Estimation of the unreacted CAT showed that one mole of cinnamyl alcohol consumed one mole of CAT corresponding to a two electron change. The products were identified as cinnamic aldehyde and p-toluenesulphonamide[3].

Kinetics of the reaction was studied at several initial [cinnamyl alcohol] and [CAT]. When the