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The pseudo-first order rate constants for hydrolysis and methanlysls of benzoyl chloride in methanol-water solutions have been measured over the temperature range 15°-45°. The solvolyis rates have been followed by conductance measurements and the reaction product ratios determined by potentiomctric titrations after completion of the reaction. When the concentration of water in the solvent is increased, the observed solvolyis rate constant first increases to a maximum at about 0.5 water mole fraction, then decreases. The influence of solvent variation on reaction rate has been examined in terms of changes in the activation parameters. The results do not support any simple correlation between the macroscopic dielectric constant of the medium and the reaction rate constant. The effect of solvent on the enthalpies and entropies of activation has been considered in terms of the electrostatic theory and on the basis of the change in the solvent structure.

The solvolyis of benzoyl chloride has been studied in aqueous-organic mixed solvents by several investigators. However, no detailed study of the solvolyis of benzoyl chloride in alcohol-water mixtures has been undertaken. This led us to study the behaviour of this substrate in a series of methanol-water mixtures including the pure solvents, in order to understand the behaviour of the entropy and enthalpy of activation of solvolytic displacement reactions towards solvent variation. For some reactions the resulting solvent effects were discussed in terms of specific solvation of reactants and transition states. In other solvolytic reactions it was concluded that the behaviour of activation parameters towards solvent variation is determined to a large extent by the process of solvent reorganization in the activation process. In the present study, we noted that this last conclusion should especially be used to explain the results of solvolyis of benzoyl chloride in the water-rich solutions.

Materials and Methods

Benzoyl chloride (AR) was distilled and kept out of contact with light. Doubly distilled water and absolute methanol purified according to recommended procedures were used to make the solutions (v/v).

The rate of solvolyis reaction was followed conductometrically. Conductance-concentration calibration curves were constructed using standardized hydrochloric acid solutions, at several experimental temperatures and in the various solvent mixtures, for conversion of measured conductivity to molar concentrations. The range of initial concentrations suitable for the kinetic studies on the halide was determined by trial and error. In the concentration range 0.01 to 0.1 molar benzoyl chloride, kinetic results were reproducible and exhibited strictly first-order behaviour with small random experimental error.

The products of reaction were determined by acidimetry after completion of the reaction. Analysis of hydrochloric and benzoic acids in the reaction mixtures was done by potentiometric pH titration using a Corning model 12 research pH meter. The equivalence points were determined from the change in potential per 0.05 ml change in volume of reagent. Titrations were generally done at a time which exceeded at least 10 half-lives after the end of reaction while the samples were thermostated at reaction temperatures.

Results and Discussion

The pseudo-first order rate constants, \( k \) (sec\(^{-1}\)), were determined graphically from measurements covering at least the first half of the reaction. The logarithmic first order plots were strictly linear in all solvent mixtures. Table 1 shows the results of the rate measurements in methanol-water solutions at various temperatures and solvent compositions. Fig. 1 shows the dependence of the observed rate constants on solvent composition for the solvolytic reaction. It is seen that when the concentration of water in the solvent is increased, the rate constant first increases to a maximum at about 0.5 water mole fraction and then decreases. Non-linear dependence of solvolyis rate constants on solvent composition has been observed for other systems in several binary solvent mixtures.
TABLE 1 — EFFECT OF TEMPERATURE AND SOLVENT COMPOSITION ON THE OBSERVED PSEUDO-FIRST ORDER RATE CONSTANTS IN THE SOLVOLYSIS OF BENZOYL CHLORIDE IN METHANOL-WATER MIXTURES

<table>
<thead>
<tr>
<th>Water-Methanol Mole fraction (v/v) of water</th>
<th>15°</th>
<th>25°</th>
<th>35°</th>
<th>45°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol 0.00</td>
<td>1.55±0.02</td>
<td>6.65±0.03</td>
<td>9.00±0.05</td>
<td>21.0±0.3</td>
</tr>
<tr>
<td>Methanol 0.10</td>
<td>2.42±0.03</td>
<td>13.3±0.01</td>
<td>23.5±0.5</td>
<td>50.0±0.5</td>
</tr>
<tr>
<td>Methanol 0.30</td>
<td>4.00±0.05</td>
<td>18.0±0.02</td>
<td>39.5±0.5</td>
<td>75.0±0.5</td>
</tr>
<tr>
<td>Methanol 0.50</td>
<td>8.30±0.01</td>
<td>18.10±0.02</td>
<td>39.5±0.5</td>
<td>75.0±0.5</td>
</tr>
<tr>
<td>Methanol 0.70</td>
<td>18.4±0.05</td>
<td>39.5±0.05</td>
<td>75.0±0.05</td>
<td>25.0±0.5</td>
</tr>
<tr>
<td>Methanol 0.90</td>
<td>36.9±0.04</td>
<td>75.0±0.04</td>
<td>25.0±0.5</td>
<td>20.0±0.05</td>
</tr>
</tbody>
</table>

In a mixture of methanol and water the reaction of benzoyl chloride has been envisaged as shown in Eq. (1),

$\text{PhCOCl} \rightarrow \text{PhCOOH} + \text{H}_2\text{O} + \text{Cl}^-$

Hence the observed rate constant ($k_{\text{obs}}$) is the sum of the rate constants for the hydrolysis reaction ($k_a$) and the rate constant for the alcoholysis reaction ($k_w$), i.e.

$k_{\text{obs}} = k_a + k_w$  ...(2)

In order to analyse the temperature dependence of $k_{\text{obs}}$ we realize that the activation parameters $\Delta H_{\text{obs}}$ and $\Delta S_{\text{obs}}$ are composite and each is a function of $k_a$ and $k_w$ which are themselves temperature dependent. It follows from absolute rate theory that:

$\Delta H_{\text{obs}} = \ln k_{\text{obs}} = \Delta H_a + \Delta H_w  ... (3)$

and after some manipulations of Eq. (3), one obtains:

$\frac{\partial \ln k_{\text{obs}}}{\partial T} = \frac{\Delta H_a}{k_w} + \frac{\Delta H_w}{k_a}$  ...(4)

In Eq. (4) we can substitute for the ln $K_t$s to obtain

$\Delta H_{\text{obs}} = \frac{k_w}{k_a + k_w} \Delta H_a + \frac{k_a}{k_a + k_w} \Delta H_w$  ...(5)

Eq. (5) relates $\Delta H_{\text{obs}}$ to the enthalpy of activation for hydrolysis ($\Delta H_a$) and the enthalpy of activation for alcoholysis ($\Delta H_w$).

Again, from absolute rate theory, we have:

$\Delta H^2 = -RT \ln (R/N)T + T \Delta S^*$  ...(6)

where $(R/N)$ is the Boltzmann gas constant and $k$ is the Planck's constant. Substituting Eq. (6) into Eq. (5), we get:

$\Delta S^*_{\text{obs}} = \frac{k_w}{k_a + k_w} \Delta S^*_a + \frac{k_a}{k_a + k_w} \Delta S^*_w  ... (7)$

Eq. (7) can be rewritten in the form:

$\Delta S^*_{\text{obs}} = \left(\frac{k_a}{k_{\text{obs}}}\right) \Delta S^*_a + \left(\frac{k_w}{k_{\text{obs}}}\right) \Delta S^*_w$  ...(8)

Eq. (6) relates $\Delta S^*_{\text{obs}}$ to the entropy of activation for hydrolysis ($\Delta S^*_a$) and the entropy of activation for alcoholysis ($\Delta S^*_w$).

Therefore, in order to allow for a detailed examination of the thermodynamic parameters, analysis of the reaction products at the end of reaction and at each temperature and solvent composition was necessary. The relative rate constant, $\left(k_a/CH_2OH\right)$ is given simply by the relative concen-
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Analysis of the reaction products was done by potentiometric titration of the solution after the completion of the reaction and typical results of titration curves obtained at 35-0°C are shown in Fig. 2 for the different solvent compositions used in this study. If \( x \) represents the volume of the base solution equivalent to the first equivalence point in the titration curve and \( y \) represents the volume of the base solution at the second equivalence point, then \( (y-x)/x \) is the fraction of benzoyl chloride hydrolysed, \( (2x-y)/x \) is the fraction alcoholysed, and \( (y-x)/(2x-y) \) represents the reaction product ratio, \( ([\text{PhCOOH}]/[\text{PhCOOCH₃}])_{\text{t=co.}} \).

Table 2 lists the product ratios obtained at different temperatures and solvent compositions. At least triplicate experiments were made and the average errors in the product ratios were less than 2% in most cases. The extent of conversion of the ester into acid and alcohol was negligible under our experimental conditions. The results show that the relative amounts of products acid and ester, by reaction with water and with methanol, respectively, are directly proportional to the respective rate constants \( k_{\text{w}}[\text{H}_2\text{O}] \) and \( k_{\text{ROH}}[\text{ROH}] \). This experimental result favours the postulation of direct displacement by solvent.

The separation of the observed rate constants into the rate constants for hydrolysis and alcoholysis was done making use of the results of the acidimetry experiments. Energies of activation for hydrolysis and alcoholysis were found from the temperature dependence of the reaction rates according to Arrhenius equation making use of the method of least squares. Activation entropies \( \Delta S^\ddagger \) and \( \Delta S^\ddagger \) and enthalpies \( \Delta H^\ddagger \) and \( \Delta H^\ddagger \) were calculated from the respective rate constants according to absolute rate theory equations. The activation parameters calculated from the experimental data are recorded in Table 3. The high negative entropy values for both hydrolysis and alcoholysis indicate a decrease in the degree of freedom of the system as a whole when the reactants pass into the transition state and are most probably due to the freezing of solvent molecules strongly oriented around the transition state. The data in Table 3...

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**Table 2**

<table>
<thead>
<tr>
<th>Mole fraction of water</th>
<th>( ([\text{PhCOOH}]/[\text{PhCOOCH₃}])_{\text{t=co.}} ) at</th>
</tr>
</thead>
<tbody>
<tr>
<td>25°</td>
<td>35°</td>
</tr>
<tr>
<td>0·10</td>
<td>0·025</td>
</tr>
<tr>
<td>0·30</td>
<td>0·088</td>
</tr>
<tr>
<td>0·50</td>
<td>0·242</td>
</tr>
<tr>
<td>0·70</td>
<td>0·530</td>
</tr>
<tr>
<td>0·80</td>
<td>0·617</td>
</tr>
<tr>
<td>0·90</td>
<td>1·127</td>
</tr>
</tbody>
</table>

**Table 3**

<table>
<thead>
<tr>
<th>Mole fraction of water</th>
<th>( \Delta H^\ddagger ) kcal mol(^{-1})</th>
<th>( -\Delta S^\ddagger ) cal deg(^{-1}) mol(^{-1})</th>
<th>( \Delta H^\ddagger ) kcal mol(^{-1})</th>
<th>( -\Delta S^\ddagger ) cal deg(^{-1}) mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0·00</td>
<td>17·36</td>
<td>19·74</td>
<td>15·03</td>
<td>25·47</td>
</tr>
<tr>
<td>0·10</td>
<td>15·37</td>
<td>25·46</td>
<td>14·20</td>
<td>26·25</td>
</tr>
<tr>
<td>0·30</td>
<td>18·81</td>
<td>25·80</td>
<td>12·26</td>
<td>31·53</td>
</tr>
<tr>
<td>0·50</td>
<td>18·84</td>
<td>41·73</td>
<td>11·27</td>
<td>37·42</td>
</tr>
<tr>
<td>0·70</td>
<td>9·81</td>
<td>47·26</td>
<td>9·16</td>
<td>45·72</td>
</tr>
<tr>
<td>0·80</td>
<td>10·65</td>
<td>46·29</td>
<td>9·75</td>
<td>45·18</td>
</tr>
<tr>
<td>1·0</td>
<td>14·04</td>
<td>34·83</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
also show that this is more so in hydrolysis than in methanolysis. In a series of related reactions
involving moderate changes in structure or solvent the enthalpies and entropies vary, but usually not
independently. Solvent-solute interaction that, for example, leads to stronger binding between solute
and solvent molecules will lower the enthalpy; it will also, by restricting the freedom of vibration
and of rotation of the solvent molecules, lower the entropy.

The change from water to methanol involves a large decrease in ionizing power, yet the rate of
reaction is higher in pure methanol than in water. In methanol $\Delta H^*$ is higher by about 1·0 kcal
mol$^{-1}$, but $\Delta S^*$ is higher by about 9·4 cal deg$^{-1}$
mol$^{-1}$ than that in pure water. Since the ionic
charge is more concentrated at the transition state
compared to the ground state, the extent of solvation
is increased, but relatively more in hydrolysis than in
methanolysis. The increased bonding to the solvent
at the transition state results in lowering of energy
of activation; however, the decrease in the mobility
of some solvent molecules more than compensates
for the decrease in the entropy of activation and
this gives rise to a net increase in reaction rate
upon changing the solvent from water to methanol.
The abrupt change in reaction rates and activation
parameters in the highly aqueous solvents might
suggest the operation of a dual mechanism, i.e. a
bimolecular substitution and a unimolecular ioniza-
tion prepondering at high water concentration$^{9,10}$.

It can be seen that the enthalpy and entropy of
activation for hydrolysis ($\Delta H^*$ and $\Delta S^*$) exhibit a
minimum in the water rich solutions at about 0·8
water mole fraction. The depth of this minimum
relative to pure water amounts to about 4·2 kcal
mol$^{-1}$ and 12·4 cal deg$^{-1}$ mol$^{-1}$ in $\Delta S^*$. Similarly, it is also observed that the methanolysis
reaction exhibits a minimum in the methanol rich
solutions at about 0·9 methanol mole fraction.
However, the depth of this minimum relative to
pure methanol amounts to only about 1·6 kcal
mol$^{-1}$ in $\Delta H^*$ and 4·5 cal deg$^{-1}$ mol$^{-1}$ in $\Delta S^*$. These variations in the enthalpy and entropy
of activation are in general agreement with the results
in binary alcohol-water systems previously reported
for the solvolysis of tert-butyl chloride$^{9,10}$, benzyl
chloride$^{11}$ and for mono- and tri-chloroacetate
ions$^{11,12}$. This behaviour is observed not only for
activation parameters in solvolysis reactions, but also for many of the physical properties of solutes
in mixed solvents$^{13}$.

It is well known that the addition of a small
amount of methanol to water increases the structure
making power of the solution and that the extrema
in $\Delta H^*$ and $\Delta S^*$ are related to the accompanying
solvent reorganization attending the activation pro-
cess for solvolysis in binary alcohol-water systems$^{9,14}$. The results in the methanol-rich solutions point
to a similar situation where the addition of a small
amount of water to methanol increases the degree
of structuredness of the solution, although the
sensitivity of the activation parameters to the
solvent-structural effects seems to be lower in the
alcoholysis than in the hydrolysis reaction.

The results do not support any simple correlation
between the dielectric constant of the medium, $D$,
and the reaction rate constants. A linear relation
between $\log k$ and $(D - 1)/(2D + 1)$ follows from
Kirkwood’s treatment of dipole solvation by assuming
that the reagent molecules and the transition states
can be regarded as electric dipoles immersed in a
structureless medium of dielectric constant $D$
and that all non-electrostatic interactions are un-
important$^{15}$. In the present study, the transition
state has a larger dipole moment than the reactant
molecule and hence it is expected that the reaction
should be accelerated in solvents of high dielectric
constant. However, the plot of $\log k$ versus $(D - 1)/(2D + 1)$, shown in Fig. 3, shows that a linear
relation of the type mentioned holds for media
containing less than about 0·5 water mole fraction.
On extrapolation of the curve to more aqueous
media, a departure from such linearity appears to
set in fairly suddenly. Of course, solvents are not
continuous media and in the vicinity of the reacting
species individual solvent molecules would un-
doubtedly play an important role. The predictions
of the dielectric constant theory sometimes fit and
sometimes fail to fit the actual behaviour of polar
reaction$^{9,20}$. Here, it is concluded that the simple
electrostatic theory is inadequate to account for the
result for the whole range of solvent composition.
On this basis one would conclude that over the
linear portion of the curve (for media containing
less than about 0·5 water mole fraction) the
solvolysis reaction occurs in a structureless medium
and that the dielectric theory of medium effects
holds good. In the water-rich solutions, the structure
of the solvent and the increased amount of hydrogen-
bonded structures play a more important role.

References
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