For identical polar heads the effectiveness should solely depend upon the hydrocarbon chain (this can be either a side chain or one having the polar head). Hence the following orders of effectiveness are justified: CPB>TDPB>LPB; CPC>LPC; Mar oxol-OT>Manoxol-IB.

Molecules of a suppressor with a smaller polar head will crowd the double layer and its vicinity hence will be more effective, as in the case of OT> Manoxol-IB.

Different non-ionic suppressors are adsorbed on the mercury drop to different extents at a given potential. The order of effectiveness amongst the suppressors used is: Triton X-100 > Decon-90, Amido black, ethyl digoI, 2-ethoxy ethanol.

Thanks are due to Dr O. P. Bansal and Dr S. N. Srivastava for their keen interest in this work and to Dr S. N. Dubey, Principal, Agra College, Agra, for providing necessary facilities.

Notes

In this note we report the kinetics of reaction between di- and tri-substituted benzoyl chlorides with aniline in benzene. The conclusions drawn from the present study are similar to those reported by Saxena and Bose.

Aniline reacts with substituted benzoyl chlorides as shown in Eqs. (i) and (ii).

\[
\text{R.C}_6\text{H}_5\text{COCl} + \text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{R.C}_6\text{H}_5\text{CONH}C\text{H}_6 + \text{HCl}
\]

\[
\text{HCl} + \text{C}_6\text{H}_5\text{NH}_2 = \text{C}_6\text{H}_5\text{NH}_2 \text{HCl}
\]

Step (i) is the rate determining step. In order to study the reaction kinetics, standard solutions of aniline (0·04M) and substituted benzoyl chlorides (0·02M) were prepared in benzene. After equilibrating at the desired temperature (30° ± 0·1°) the solution of benzoyl chloride (5 ml) was mixed with the solution of aniline (5 ml) in a reaction vessel containing benzene (10 ml), and the reaction mixture shaken well. The final concentrations of benzoyl chloride and aniline in the reaction mixture were 0·01M and 0·005M respectively.

The precipitate of aniline hydrochloride formed after definite intervals of time was filtered off through Gooch crucible. The reaction vessel was washed twice with benzene and finally with distilled water. To the washings and the precipitate was added 5 ml of 6N nitric acid to dissolve the precipitate completely. The chloride was estimated by Volhard's method.

A slightly modified bimolecular velocity constant equation was used for calculating \( k \) values for this reaction. If \( a \) is the initial concentration of substituted benzoyl chloride, \( 2a \) that of aniline and if \( x \) is the amount of substituted benzoyl chloride which reacted in time \( t \), then the concentration of aniline that reacted should be \( 2x \).

Thus \( \frac{dx}{dt} = k (a-x)(2a-2x) \), whence

\[
k = \frac{1}{120} \left( \frac{1}{100Z} - \frac{1}{100} \right) a
\]

where \( k \) is the velocity constant in litre mole\(^{-1}\) sec\(^{-1}\), \( t \) is the time in min and \( Z \) is the percentage conversion. The bimolecular rate constants have been found to be constant up to 70\% conversion. The energy of activation was calculated by 'least square method' and also from the Arrhenius plot.

It is evident from the data given in Table 1 that there is marked variation of the energy of activation with the substituent. The energy of activation

<table>
<thead>
<tr>
<th>Benzoyl chloride</th>
<th>( \log A )</th>
<th>( \Delta E )</th>
<th>( \log_{10} (R_a) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>litre mole(^{-1}) sec(^{-1})</td>
<td>( \sqrt{M \times 10^8} )</td>
<td></td>
</tr>
<tr>
<td>2,4-Dichloro-</td>
<td>4.41</td>
<td>+210</td>
<td>1.8190</td>
</tr>
<tr>
<td>3,5-Dinitro-</td>
<td>4.25</td>
<td>-330</td>
<td>2.6224</td>
</tr>
<tr>
<td>3-Nitro-4-chloro-</td>
<td>4.19</td>
<td>+60</td>
<td>2.6870</td>
</tr>
<tr>
<td>3,4-Dimethoxy-</td>
<td>4.61</td>
<td>+360</td>
<td>1.5699</td>
</tr>
<tr>
<td>3,4,5-Trimethoxy-</td>
<td>4.42</td>
<td>+100</td>
<td>1.5650</td>
</tr>
<tr>
<td>3-Methoxy-4-ethoxy-</td>
<td>4.48</td>
<td></td>
<td>1.3406</td>
</tr>
</tbody>
</table>

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when plotted against log $k_0$ gives a linear plot with the slope $\approx 2.303 RT$, indicating that for these compounds the entropy of activation is constant. The variations in the velocity constant at a given temperature caused by different substituents in benzyol chloride are due to the chances in the energy of activation.

The energy of activation of benzyol chloride being $7600 \text{ cal g}^{-1} \text{ mole}^{-1}$, the changes in activation energy ($\Delta E^*$) caused by various substituents present in substituted benzyol chlorides have been calculated and the results obtained are given in Table 2. The theoretical values for the activation energies of di- and tri-substituted benzyol chlorides have been calculated by the addition of the value of $\Delta E$ for the substituent groups to the value of activation energy of benzyol chloride. The value of 2,4-dichlorobenzyol chloride and 3,4,5-trimethoxybenzyol chloride have been calculated in the following manner:

(i) Energy of activation of 2,4-dichlorobenzyol chloride $7600 - 900 = 6700 \text{ cal g}^{-1} \text{ mole}^{-1}$ (experimental value $6900 \text{ cal g}^{-1} \text{ mole}^{-1}$)

(ii) Energy of activation of 3,4,5-trimethoxybenzyol chloride $7600 - 200 - 900 = 6500 \text{ cal g}^{-1} \text{ mole}^{-1}$ (experimental value $6800 \text{ cal g}^{-1} \text{ mole}^{-1}$).

Thus experimental values of energy of activation of di- and tri-substituted benzyol chlorides are in good agreement with the calculated values. It is interesting to compare the effect of substituents in aniline and in benzyol chloride on the reaction rate. It is observed (Table 2) that ortho-chloro group in the benzyol chloride decreases the energy of activation, whereas the o-chloro group in aniline increases the energy of activation. In the case of para-methoxybenzyol chloride the energy of activation is increased by $900 \text{ cal mole}^{-1}$. As the methoxy group increases the quinonoid structure in both the initial and transitional state of benzyol chloride, it will therefore increase the activation energy, which has actually been observed.

The plot of dipole moments of substituted benzyol chlorides versus energies of activation is linear in conformity with the observations of Nathan and Watson and Grant and Hinselwood.

This reaction studied also fits well with Hamnett's equation. The positive slope value ($+1.406$) for the Hamnett plot indicates that the reaction is aided by the electron withdrawing group in benzyol chloride.