Linear Free Energy Relationships in Solid State Reactions: Part III—Reactions of Zinc Acetate with Aniline Salts

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Reactions between anhydrous zinc acetate and a series of substituted aniline hydrochlorides have been studied in the solid state. The products, characterized by elemental analyses and spectral data are $\text{ZnCl}_2 \cdot 2(\text{amine})$. The kinetics of these reactions have been studied by the mass loss method. Energy of activation values are 26.9, 38.9, 57.7, 144.7, 92.8, 117.4, 97.4, 162.2 and 186.5 kJ mol$^{-1}$ for $X=2$-Cl, 3-Cl, 4-Cl, 4-I, 3-0CH$^-$, 4-F, H, 4-CH$^-$, and 4-OCH$^-$, respectively. A plot of energy of activation with Hammett $\sigma$ constants of the substituents is linear. Unsubstituted aniline salt and 4-iodoaniline hydrochloride show deviations which have been interpreted in terms of differences in crystal structure and size of these reactants. The reactions proceed by the formation of an adduct, which then decomposes with the loss of gaseous acetic acid.

The Hammett equation$^1$ has been successfully used for the correlation of the reactivities of disubstituted benzene derivatives with the position and nature of substituents. The equation, extensively used in organic reactions, has recently been shown to correlate the reactivities of inorganic complexes containing benzene derivatives with the substituent parameters$^2$. The applicability of the relationship to solid-solid reactions is expected to give valuable information about the nature and mechanism of these reactions also. In the reactions of aniline hydrochlorides with cobalt acetate in the solid state, studied by the capillary and mass loss methods$^3,4$ the Hammett equation applies successfully. Presently we have examined the applicability of Hammett equation to the solid-solid reactions of zinc acetate with aniline hydrochlorides.

In order that the kinetic data may be correlated, it is necessary that the structure, composition and bonding of the reactants throughout the series is similar and the same holds for the products. A large number of zinc halide complexes with aromatic amines, such as $\text{ZnY}_2 \cdot 2(\text{amine})$ where $Y=\text{Cl}$, Br, 1 and $X=2$-CH$^-$, 4-CH$^-$, 2-OCH$^-$, 4-OCH$^-$, 2-Cl, 3-Cl, 4-Cl, 2-Br, 3-Br and 4-Br etc. have been reported in the literature$^5-8$. All the salts are centrosymmetric except that with aniline hydrochloride, which is non-centrosymmetric. The products as characterized by spectral and elemental analyses show the same composition $\text{ZnCl}_2 \cdot 2(\text{amine})$ and are tetrahedral in which $\text{Zn}-\text{N}$ bond is predominantly covalent$^9$. X-ray studies of $\text{ZnCl}_2 \cdot 2(\text{C}_6\text{H}_5\text{NH}_2)$ and $\text{ZnCl}_2 \cdot 2(4$-CH$^-$C$_6$H$_5$NH$_2$) and data on heats of coordination of the complexes show that they are isostructural$^{10}$.

Materials and Methods
Zinc acetate (AR) was dried at 383K overnight (Found: Zn, 35.1. Calc. Zn, 35.7%). Aniline hydrochlorides, prepared by passing dry hydrogen chloride gas through solutions of amines in dry ethanol, were purified by repeated recrystallizations and the purity checked by elemental analyses and melting points. All the reactants were powdered and sieved to collect of fixed size (44 μ). The solution phase reaction products were prepared by known methods.

Kinetics
The measurement of kinetic data for solid state reactions is difficult. The reactants were chosen in such a manner that they either give a coloured product or that one of the products was volatile. Acetic acid was the only gaseous product, and so the mass loss gave a measure of the extent of reaction. In a typical kinetic run zinc acetate (0.001 mol) and aniline hydrochloride (0.002 mol) were separately weighed and thermostated for about 10 min. They were mixed with special care to get the best possible homogeneity while exerting minimum of pressure on the reactants. This mixture was transferred to a glass bucket, which was connected to a five decimal electrical balance. The change in weight with time was monitored using fixed particle size of all the reactants (44 μ).

Results and Discussion
To determine compounds present in the gaseous products in the solid-solid reactions between anhydrous zinc acetate and substituted aniline hydrochlorides, the volatilized material was success-
ively passed through three towers containing (i) anhydrous copper sulphate (to detect water), (ii) freshly prepared lime water (for carbon dioxide) and (iii) silver nitrate solution (for halogen). These tests gave negative results for the presence of water, halogen and carbon dioxide in the gases evolved on the reaction.

The stoichiometry of the reactions was established by mixing the reactants in molar ratios of 1:1, 1:2 and 1:4 and allowing them to go to completion in a thermostat (373 K), till no further mass loss was detected. As a representative case the reaction of zinc acetate with 2-chloroaniline hydrochloride is reported. After the completion of reaction, it was found that 1:1 mixture contained unreacted zinc acetate whereas 1:4 mixture contained unreacted aniline salt. TLC of the 1:2 mixture showed that none of the reactant was present in the product and that it was a single compound. The amount of acetic acid evolved was estimated acidimetrically. The evolved gas was bubbled through a solution of sodium hydroxide using dry nitrogen as the carrier gas. The loss of acetic acid due to acetic acid at any time. In each case the reactants were taken in the molar ratio of 1:2, so that the measured mass loss not only gave a measure of the extent of reaction, but also a direct measure of \( \alpha \), the fraction of the reactants consumed. Plots of \( \alpha \) versus time for different reactions at different intervals of time and at different temperatures for fixed particle size of the reactants were drawn. These plots may be divided into two groups. One group showed an induction period followed by an acceleratory region and decay near the completion \((X=H, 2-Cl, 3-Cl, 4-Cl\) and \(3-OCH_3\)) (see Fig. 1). The other group showed a deceleratory behaviour throughout \((X=4-I, 4-F, 4-CH_3\) and \(4-OCH_3\)) (see Fig. 2).

The interpretation of measured isothermal kinetic data has frequently been based on comparison of excellence of fit of such measured values with the requirements of rate equations derived from different geometric models. In the reactions re-

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**Table 1 — Microanalytical Data of Solid Phase Reaction Products, ZnCl_2·2(XC_6H_4NH_2) Found (calc), (%)**

<table>
<thead>
<tr>
<th>X</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Zn</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Cl</td>
<td>36.1(37.0)</td>
<td>3.6(3.1)</td>
<td>7.6(7.2)</td>
<td>16.4(16.8)</td>
<td>18.5(18.2)</td>
</tr>
<tr>
<td>3-Cl</td>
<td>35.0(37.0)</td>
<td>4.2(3.1)</td>
<td>7.8(7.2)</td>
<td>17.0(16.8)</td>
<td>18.0(18.2)</td>
</tr>
<tr>
<td>4-Cl</td>
<td>37.5(37.0)</td>
<td>4.3(3.1)</td>
<td>7.6(7.2)</td>
<td>16.8(16.8)</td>
<td>18.4(18.2)</td>
</tr>
<tr>
<td>4-I</td>
<td>25.8(25.2)</td>
<td>2.7(2.1)</td>
<td>5.0(4.9)</td>
<td>11.5(11.4)</td>
<td>12.8(12.4)</td>
</tr>
<tr>
<td>4-F</td>
<td>41.8(40.4)</td>
<td>2.8(3.4)</td>
<td>8.6(8.1)</td>
<td>18.2(18.3)</td>
<td>19.5(19.9)</td>
</tr>
<tr>
<td>H</td>
<td>45.3(45.0)</td>
<td>4.6(4.4)</td>
<td>8.7(8.8)</td>
<td>20.0(20.4)</td>
<td>22.0(22.2)</td>
</tr>
<tr>
<td>3-OCH_3</td>
<td>43.6(43.9)</td>
<td>5.1(4.7)</td>
<td>6.9(7.8)</td>
<td>17.5(17.1)</td>
<td>18.8(18.6)</td>
</tr>
<tr>
<td>4-CH_3</td>
<td>50.2(48.2)</td>
<td>4.4(5.2)</td>
<td>8.6(8.0)</td>
<td>18.5(18.8)</td>
<td>19.3(20.4)</td>
</tr>
<tr>
<td>4-OCH_3</td>
<td>43.4(43.9)</td>
<td>5.3(4.8)</td>
<td>6.9(7.8)</td>
<td>17.3(17.1)</td>
<td>18.2(18.6)</td>
</tr>
</tbody>
</table>
ported, Eq. (1) fitted the data throughout the range of α, in which the reactions were studied, with a correlation coefficient greater than 0.99. All other equations gave a poor fit. According to Galwey\textsuperscript{11} the magnitude of $E_a$ can be accepted as a valuable method for comparing reactivities of solids. Moreover, the calculated magnitudes of $E_a$ are comparatively insensitive to the particular rate equation used for the kinetic analysis, provided that power laws are based on $(kt)^n$ and not $kt^n$.

$$\alpha^n = kt \quad \ldots (1)$$

The values of energy of activation ($E_a$) have been calculated from the Arrhenius plots. The values are 26.9, 38.9, 57.7, 144.7, 92.8, 117.4, 97.4, 162.2 and 186.5 kJ mol$^{-1}$ for $X = 2$-Cl, 3-Cl, 4-Cl, 4-I, 3-OCH$_3$, 4-F, H, 4-CH$_3$ and 4-OCH$_3$, respectively. A comparison of $E_a$ values shows that the relative order of reactivity is: 2-Cl > 3-Cl > 4-Cl > 3-OCH$_3$ > H > 4-F > 4-I > 4-CH$_3$ > 4-OCH$_3$.

Electron withdrawing substituents enhance the reactivity and electron donors increase the basicity of nitrogen. The greater reactivity of 2-chloroaniline can be attributed to the ortho effect.

To test the validity of Hammett equation, the constants $\sigma$, $\sigma_R$ and $\sigma_I$ were chosen. Regression analysis showed that $\sigma_R$ and $\sigma_I$ give erratic plots while the best results are obtained using $\sigma$ (Fig. 3). The plot is linear with a slope of $-208.9$ kJ mol$^{-1}$.

Aniline and 4-iodoaniline hydrochlorides showed significant deviations from the Hammett plot. The high value of $E_a$ for 4-iodoaniline hydrochloride is due to the bulky iodo substituent, which decreases the effective contact area between the reactants. For the unsubstituted salt, much lower value of $E_a$ is attributed to a better contact between the reactants and also due to the presence of polar axis which enhances reactivity\textsuperscript{12}. The negative slope shows that as the acidity of the anilium ion increases, the rate of the reaction is enhanced.

To understand the sequence of chemical steps taking place at the zinc acetate/aniline hydrochloride phase boundary, the following observations are significant.

(i) The values of heat of addition, for reactions giving products $\mathrm{ZnX_2 \cdot 2(amine)}$, are almost independent of the nature of anion and the position of the substituent group on the benzene ring\textsuperscript{10}. 

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*Fig. 1—Kinetic plots for the reaction between zinc acetate and 2-chloroaniline hydrochloride at different temperatures*

*Fig. 2—Kinetic plots for the reaction between zinc acetate and 4-toluidine hydrochloride at different temperatures*

*Fig. 3—Plot of Hammett 'o' constant against energy of activation*
(ii) Reactions of anhydrous zinc chloride with p-toluidine and p-chloroaniline (amines which are solid at room temperature) have also been investigated. The reactions are very fast and are complete immediately on mixing. The products have been identified to be the adducts by elemental analyses and spectral studies.

These two facts along with the observation that the IR spectra exhibit bands due to Zn–Cl and R–NH$_2$ groups and no bands due to free or coordinated NH$_2$ groups indicate the formation of an intermediate adduct (XC$_6$H$_4$NH$_3$)$_2$/Zn(CH$_3$COO)$_2$Cl$_2$), which decomposes to give the final product.

To see whether these reactions are true solid-solid reactions or involve certain features of the solid-gas reactions, the effect of presence of gases obtained from the thermal decomposition of the reactants on the rate of reaction was studied. Reaction of zinc acetate with aniline hydrochloride exposed to dry hydrogen chloride vapours for 5 min gave a rate constant of 0.825 g h$^{-1}$. In the reaction of zinc acetate exposed to vapours of acetic acid with unexposed aniline hydrochloride, the rate constant is 0.584 g h$^{-1}$, as compared to 1.018 g h$^{-1}$ for unexposed reactants. Thus, both adsorption of HCl on aniline hydrochloride and of CH$_3$COOH on zinc acetate has a retarding effect. This is because the adsorbed gases form an envelope around the reactants, and decrease the effective contact between them. Thus the experiments provide further proof that the reactions occur in the solid state.

References