# HEATS OF REACTION BETWEEN ANILINE AND FORMALDEHYDE BY SOLUTION CALORIMETRY: REACTION IN NEUTRAL MEDIUM

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ABSTRACT

The enthalpies of reaction between aniline and HCHO at various molar proportions under neutral conditions were determined by solution calorimetry. These measurements are new in the field of aniline and HCHO condensation polymers. The specific heats of the products formed were determined by differential scanning calorimetry and were used in the enthalpy calculations. Plots of enthalpy of reaction calculated with respect to aniline and HCHO vs. different A/F molar ratios were made. From the enthalpy data it appears that the reactions between different A/F molar ratios yield different products.

INTRODUCTION

The enthalpy data for the addition polymerization reactions are abundantly available in literature while similar data on condensation polymerization reactions are scarce. The present experimental estimation of the heat of condensation reactions of aniline (A) and HCHO (F) is expected to fill this gap to some extent. These resins find vast application as fuels in the field of rocket propellants [1] and are used as additives to improve the thermal properties of some thermosetting resins like novalacs [2]. Formaldehyde reacts spontaneously with aniline producing a variety of products including some resinous materials, viz. *N*-hydroxymethylaniline, methylene–aniline (Schiff base) and 1,3,5-triphenylhexahydro-*sym.*-triazine (anhydroformaldehydeaniline) [3]. However, the nature of the products formed depends strongly on the molar ratios of A and F reacted and also upon the pH of the medium [4]. To understand the mechanism of the formation of these compounds it is desirable to have full information regarding the enthalpy of these reactions. The only reported work available on the enthalpy of reaction between A and F is by Frey [3] for 1:1, 1:1.2 and 1:1.4 A/F molar ratios in acid medium, which is open to question for its high value. In the present investigation the main objective was to estimate the enthalpy of reaction covering a complete range of A/F molar proportions in neutral

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medium, so that a good understanding of the nature of the resulting products could be obtained. Additional experiments such as determination of the specific heat of the products formed and correction for F loss during the reaction were carried out to minimize the errors involved in the enthalpy determinations.

EXPERIMENTAL

*Chemicals*

A.R. aniline (B.D.H.) was twice distilled over zinc dust and the fraction of the distillate was collected between 183 and 184°C. Formaldehyde solution (B.D.H. assay 37–41% w/v) for which the exact w/v% was accurately determined by sodium sulfite method [5] was used in the experiments. Aqueous HCl and NaOH solutions in double-distilled water were prepared from A.R. (B.D.H.) samples.

*Apparatus and procedure*

Enthalpy measurements were carried out by solution calorimetry which is schematically shown in Fig. 1. It consists of a Dewar flask well insulated on all sides with asbestos powder and an exact fitting perspex cover with holes drilled in it for the insertion of a stirrer, thermocouple and the stem of the glass bulb. This whole assembly served as the reaction vessel. A stirrer (Remi, model L-56) rotating at a constant speed of 2000 r.p.m. and fitted with teflon blades was used. A Corning glass rod with a pointed tip was inserted into the glass tube for the purpose of breaking the bulb. The temperature of the reaction was measured by a teflon-coated two-junction chromel–alumel thermocouple having an outer diameter of 0.01 in.
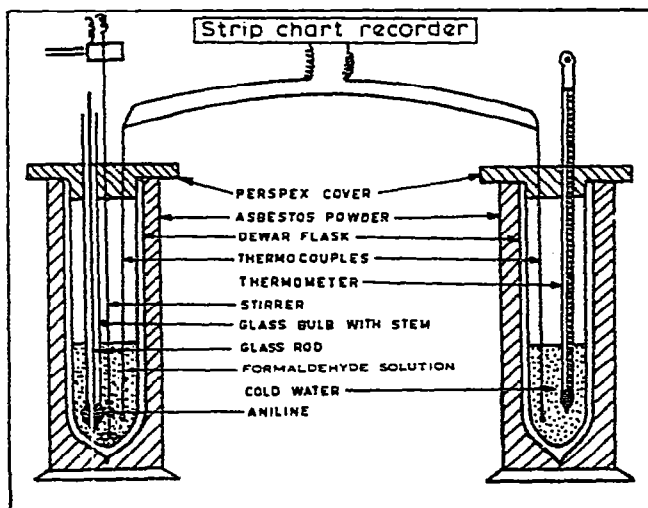


Fig. 1. Calorimeter assembly.

(Omega, U.S.A.). The thermocouple beads were dipped in Hg contained in thin tubes of 0.5 cm outer diameter. The temperature sensitivity of the thermocouple was 0.0205 mV K$^{-1}$. The cold junction of the thermopile was dipped in another Dewar flask containing cold water maintained at a constant temperature. The thermocouples were calibrated by checking the melting points of standard materials. The mV output was fed to a strip chart recorder (Omniscribe, Digital Electronics Ltd., Bombay). By keeping the sensitivity of the recorder pen at 0.5 mV, the temperature rise could be read accurately up to 0.0025°C.

A known quantity of A was placed in the glass bulb such that the volume of the liquid did not exceed that of the bulb and no liquid adhered to its stem. All weighings were done on a semi-micro single-pan Mettler balance accurate up to 0.1 mg. A known volume of F solution required to react with A in the desired A/F ratio was taken in the Dewar flask into which a known amount of water was added so that the bulb always dipped into it. The volume of water added was adjusted so that the total volume of A, F and extra water added was always maintained at 90 ml. The whole assembly containing the reactants along with stirring was allowed to attain thermal equilibrium before the start of the experiment. Upon pressing the rod downwards, the tip broke open the bulb, releasing A into the F solution which was stirred continuously. The increase in temperature of the reaction system, and hence its mV output, was recorded so that a time–temperature plot could be obtained. By recording the cooling curve, the heat transfer coefficient of the system with the surroundings could be determined.

Experimental measurements were carried out at a temperature of 298 ± 0.05 K, for 4:1, 2:1, 1:1, 1:2, 1:3, 1:4, 1:4.5, 1:4.75, 1:5 and 1:7 A and F molar ratio reactions. The energy equivalent of the calorimeter assembly including all its contents along with glass debris after breaking the bulb, was determined by measuring the heats of neutralization of HCl with NaOH by taking HCl in the bulb and NaOH in the Dewar flask. The molalities of the NaOH and HCl solutions used were 0.05000 ± 0.00005 mole kg$^{-1}$ and 0.010000 ± 0.00005 mole kg$^{-1}$, respectively. Precautions were taken to minimize carbon dioxide contamination while preparing the solutions by using freshly boiled double-distilled water and avoiding contact with air. Using the value of heat of neutralization ($\Delta H_N$) as −(62.840 ± 0.0980) kJ mole$^{-1}$, the energy equivalent of the empty calorimeter was found to be 825.93 ± 0.12 J K$^{-1}$.

*Calculation and auxiliary data*

Figure 2 shows a typical time–temperature plot, where $T_1$, $T_2$, $T_3$ are the initial, maximum and final temperatures of the system at times $t_1$, $t_2$ and $t_3$ corresponding to fore, reaction and after periods, respectively. The accurate temperature rise accounting for the heat loss to the surroundings was calculated using the integrated form of Newton's cooling law. The mean rate of change of temperature in the fore period of the reaction was found to be zero. The heat balance equation for the
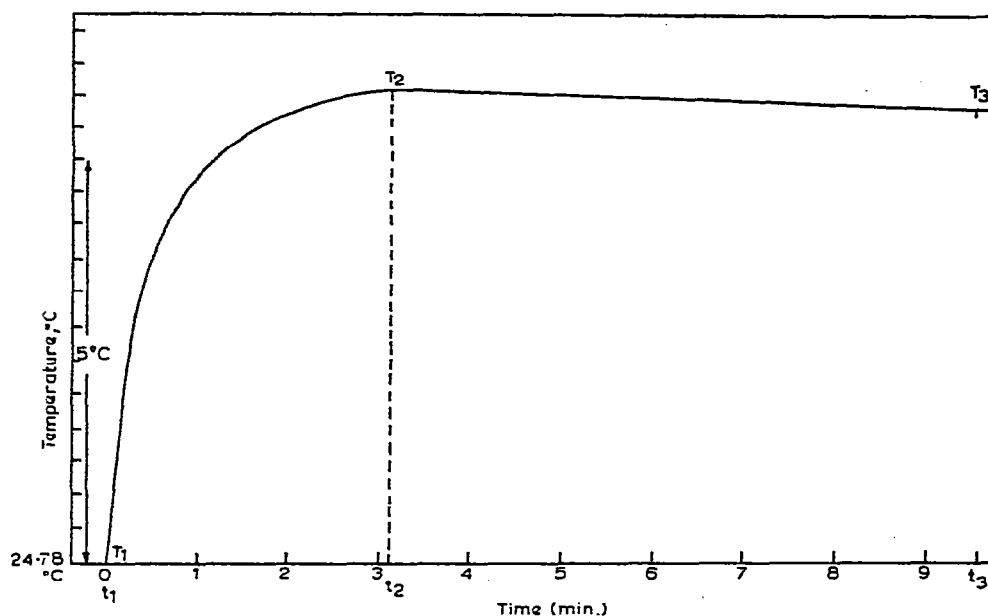
Fig. 2. A typical time–temperature plot for the A and F reaction. A : F = 1 : 7: weight of aniline = 8.5508 g: volume of water = 34.4 ml: volume of formaldehyde solution = 47.2 ml.

calorimetric system can be written as

$$\Delta H_x = \Delta T(W + m_1 + m_2 + m_3 C_{p_1} + m_4 C_{p_2})$$

where $\Delta H_x$ is the heat produced in joules for the specified amount of A and F taken, $\Delta T$ is the corrected temperature rise in °C, $W$ is the energy equivalent of the calorimetric system, $m_1$ is the weight of water added to make the total volume 90 ml and the specific heat of water = 4.184 J °C$^{-1}$ g$^{-1}$, $m_2$ is the weight of unreacted F plus the weight of water in the F solution plus the weight of water produced during the reaction (the specific heat of this mixture was taken as 4.184 J °C$^{-1}$ g$^{-1}$), $m_3$ and $C_{p_1}$ are the weight and specific heat (J °C$^{-1}$ g$^{-1}$), respectively, of the solid residue produced, $m_4$ and $C_{p_2}$ are the weight and specific heat, respectively, of the mixture of unreacted aniline and the solid product for 4:1 (A/F) composition. The term $m_4 C_{p_2}$ vanishes for all molar proportions of A and F except for 4:1 composition where a certain amount of unreacted aniline remains, while the term $m_3 C_{p_1}$ vanishes for 4:1 composition alone.

$m_2$ and $m_3$ were experimentally determined as follows. For any desired A/F ratio A and F were reacted in a separate glass container taking exactly the same quantities of A and F as taken in the Dewar flask for that desired A/F ratio. After completion of reaction the contents were completely dried in an incubator at 50°C. The weight of the dry residue corresponded to $m_3$ while $m_2$ corresponded to the weight of water produced during the reaction, water present in the F solution and unreacted F. The above determination of $m_2$ and $m_3$ is not applicable to 4:1 A/F ratio where a

TABLE 1

Specific heat data of the solid compounds obtained from the reaction between A and F taken in different molar proportions

| A/F molar ratio | Specific heat (25–30°C) (J deg$^{-1}$ g$^{-1}$) |
|---|---|
| 1:1 | 1.0736 ± 0.002 |
| 1:2 | 1.2652 ± 0.002 |
| 1:3 | 1.2749 ± 0.002 |
| 1:4 | 1.0845 ± 0.002 |
| 1:4.5 | 0.9728 ± 0.002 |
| 1:4.75 | 1.0210 ± 0.002 |
| 1:5 | 0.8648 ± 0.002 |
| 1:7 | 0.8619 ± 0.002 |
| 2:1 | 1.2749 ± 0.002 |
| 4:1 [a] | 1.2811 ± 0.002 |

[a] Including the unreacted aniline.

certain amount of A is left behind. In this case the weight ($m_4$) and the specific heat ($C_{p_2}$) were determined for the solid product mixed with aniline.

All specific heat measurements were carried out on a Dupont DSC model 990, with sapphire ($Al_2O_3$) as the standard material, and the measurements were carried out as described in the manufacturers' instructions. The data are presented in Table 1.
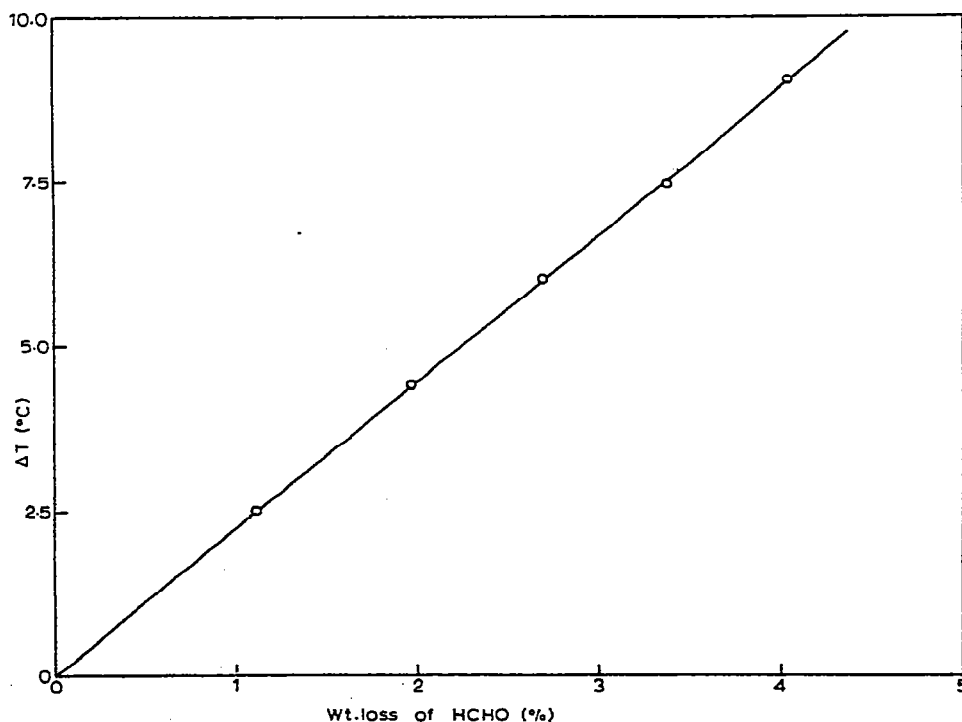


Fig. 3. Dependence of the HCHO weight loss on the temperature rise of the reaction mixture.

As the reactions between A and F are exothermic, a certain amount of F is likely to escape from the reaction mixture during the reaction period. The correction for the loss of F was determined as follows. It is a well-established fact that anhydroformaldehyde aniline (AFA) is the only product [6] formed when A and F are reacted in 1:1 molar proportion. Taking this into consideration, different amounts of A and F corresponding to 1:1 molar ratio were reacted in a Dewar flask such that different temperature rises for the same molar proportion of A:F were recorded. Similar experiments were carried out in a separate glass container taking the exact quantities of A and F as were taken in the Dewar flask and the amount of AFA formed was quantitatively estimated. From the difference in weight obtained between the experimental and the expected value, the amount of escaped F could be calculated. A plot was obtained between the temperature rise and the weight percentage of F escaped from the above experiment. The plot shown in Fig. 3 was used to determine the F loss in any experiment.

RESULTS AND DISCUSSION

The enthalpies of reaction for different stoichiometries of A and F were measured experimentally and are listed in Table 2. When the concentration of A was higher than F, the limiting concentration of F was attained at 2:1 molar proportion since 4:1 A–F ratio reaction also gives the same enthalpy value when calculated with respect to F alone. Similarly, when the concentration of A is lower than F, the limiting ratio is attained at 1:5, after which the enthalpy of reaction remains constant with respect to A. In the case of 4:1 A–F reaction a mixture of aniline and solid residue is obtained and the unreacted aniline was removed by steam distillation. Upon analysis the solid residue was identified as $NN'$-diphenyldiaminomethane. In the case of 1:1 and 2:1 A–F stoichiometric reactions (in neutral medium) the

TABLE 2

Data on heats of reaction between A and F

| Molar ratio of A:F | $\Delta H_r$ values (kJ mole$^{-1}$) of | |
|---|---|---|
| | A (at 298.15 K) | F (at 298.15 K) |
| 4:1 | 22.1712 ± 0.0011 | 88.6707 ± 0.0006 |
| 2:1 | 44.3598 ± 0.0014 | 88.6689 ± 0.0010 |
| 1:1 | 57.5575 ± 0.0011 | 57.5277 ± 0.0001 |
| 1:2 | 66.7621 ± 0.0015 | 33.3644 ± 0.0001 |
| 1:3 | 68.8400 ± 0.0016 | 22.9379 ± 0.0001 |
| 1:4 | 65.0780 ± 0.0012 | 16.2559 ± 0.0001 |
| 1:4.5 | 72.7141 ± 0.0007 | 18.8363 ± 0.0001 |
| 1:4.75 | 77.0135 ± 0.0015 | 16.2892 ± 0.0001 |
| 1:5 | 82.2513 ± 0.0006 | 16.4503 ± 0.0001 |
| 1:7 | 82.2478 ± 0.0011 | 11.7412 ± 0.0001 |

compounds reported are AFA [3] and $NN'$-diphenyldiaminomethane [7], respectively. In the present work, the formation of these compounds in their respective molar reactions of A–F was confirmed both by spectral and elemental analysis. The values of enthalpy of reaction [$\Delta H_r^0(298.15$ K)] of 1:1 and 2:1 A–F reactions are found to be $-(44.3596 \pm 0.0060)$ kJ mole$^{-1}$ and $-(172.6741 \pm 0.0044)$ kJ mole$^{-1}$, respectively.

For other stoichiometric reactions, except those of 4:1, 2:1 and 1:1 molar ratios of A–F reactions, the products obtained have not been fully analyzed. However, in order to undertake a comparative study of 4:1 to 1:7 A–F stoichiometric reactions, the heats of reactions were calculated separately with respect to A and F for each of the reactions. Figure 4 shows the plot of $\Delta H_r^0$ values calculated separately with respect to A and F vs. various A–F molar ratios. This was carried out to get some idea of the approximate value of the A–F ratio which would give the technically important thermoplastic A–F polymer. Since an increase in the value of $\Delta H_r^0$ kJ mole$^{-1}$ calculated with respect to A is obtained when the A–F molar ratio is increased, it is obvious that a decrease in $\Delta H_r^0$ values calculated with respect to F when the A–F ratio is increased should be observed. However, between 1:4 and 1:5
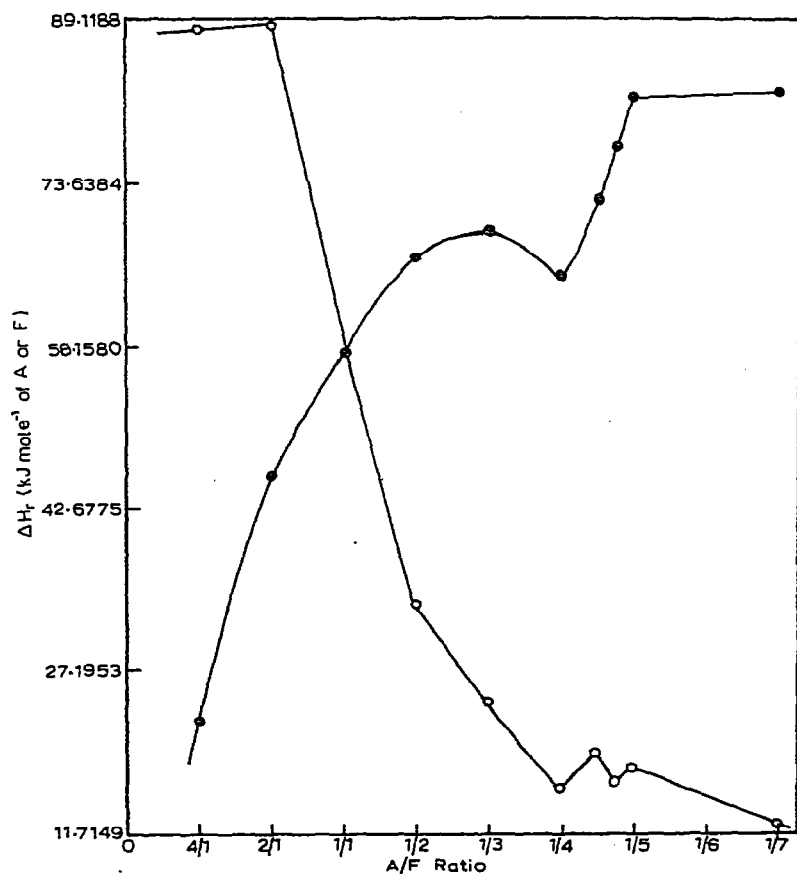


Fig. 4. Dependence of $\Delta H_r$ on the A/F ratio. ●, $\Delta H_r$ kJ mole$^{-1}$ of A; ○, $\Delta H_r$ kJ mole$^{-1}$ of F.

molar ratios of A and F there is an increase in $\Delta H_r^0$ both with respect to A and F. The exothermicity of the reactions in this region is observed to be very high and it is in this region that sticky polymeric products are obtained and hence a higher heat release could be speculated.

Since the $\Delta H_r^0$ values calculated with respect to A and F are different for different stoichiometric reactions from 2:1 to 1:5, this implies that the compounds formed in each of these reactions must be different. However, the chemical nature of these products is currently under investigation.

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