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A THERMOCHEMICAL STUDY ON THE REACTIONS OF ANILINE WITH FORMALDEHYDE IN THE PRESENCE OF ACID MEDIUM

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ABSTRACT

Using thermochemical parameters, the reaction course and the products of the reactions between aniline and formaldehyde using molar ratios of 4 : 1, 2 : 1 and 1 : 1 in the presence of acid medium have been analysed. Data on ΔH_f^0 and ΔH_r^0 were obtained experimentally by adopting combustion and solution calorimetry: theoretical data were obtained by Benson's thermochemical approach. The calculated values for the different possible structures have been compared with the experimental values of the reaction products. Thus, 4,4′-diaminodiphenylmethane has been deduced as the product for the 4 : 1 and 2 : 1 aniline: formaldehyde reactions and poly-anhydro-*p*-aminobenzylalcohol for the 1 : 1 reaction. The structure of the products were further confirmed by spectral methods. Inferences from thermochemical data were found to agree with spectral information as well as that reported by other authors.

INTRODUCTION

Reactions of aniline (AN) with formaldehyde (F) in the presence of acid catalysts yield high polymeric resinous materials. Several studies have been reported on the effect of pH, stoichiometry, nature of reaction medium, etc. on reactions conducted both in the presence and absence of acid catalysts [1,2]. Kishore and Santhanalakshmi [3,4] have studied the condensation reactions of AN and F in the absence of acid catalysts at different molar proportions and correlated the formation and structure of the reaction products with the exothermicities of these reactions. However, the products obtained from the AN–F reactions conducted in the presence of acid catalysts are infusible and insoluble materials which makes structural elucidations difficult. Also, little is known regarding the mechanistic aspects when the stoichiometries of AN and F are changed in a regular manner: in particular, little is known about the thermochemical properties. The main objective of the present investigation is to obtain a complete set of thermochemical data for reactions using 4 : 1, 2 : 1 and 1 : 1 AN/F molar ratio conducted in the presence of acid catalysts by utilising combustion and

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solution calorimetric techniques. Spectral analysis is also undertaken to check the thermochemical characterisation.

EXPERIMENTAL

Materials

Aniline (B.D.H. Analar), fractionally distilled over zinc dust at 183–184°C was used. Formaldehyde solution (B.D.H. assay 37–41% w/v), whose exact w/v% value was determined by the sodium sulfite method [5], was used as obtained. Conc. hydrochloric acid (B.D.H. Analar) with specific gravity 1.18 was used for preparing aqueous dilute solutions.

After neutralising the acid, the solid compounds obtained from the reactions using 4 : 1, 2 : 1 and 1 : 1 AN/F were separated, dried and subjected to analyses as described.

TLC studies

The solid residues obtained from the reactions using 4 : 1 and 2 : 1 AN/F were soluble in benzene. The solutions were subjected to TLC by the standard method. Both the products gave only single spots with the same R_f value. The R_f value was found to be 0.20 ± 0.01. In the case of the reaction using 1 : 1 AN/F, the product obtained was resinous in nature and therefore TLC analysis could not be performed.

Elemental analysis

A Perkin-Elmer Coleman carbon–hydrogen analyser instrument was used for C and H analyses. The procedure and method of operation were carried out as described in the manufacturer's manual. The percentage of nitrogen

TABLE 1

Elemental analysis data of AN and F reaction products

Element	I($C_{13}H_{14}N_2$)		II($C_{13}H_{14}N_2$)		III(C_7H_7N)	
	Exptl. (%)	Calcd. (%)	Exptl. (%)	Calcd. (%)	Exptl. (%)	Calcd. (%)
C	77.77 ± 0.02	78.79	78.12 ± 0.02	78.79	79.92 ± 0.01	80.00
H	7.05 ± 0.06	7.07	7.08 ± 0.06	7.07	6.69 ± 0.06	6.67
N	14.12 ± 0.03 [a]	14.14	14.14 ± 0.03 [a]	14.14	13.32 ± 0.03 [a]	13.33
	14.00 ± 0.2 [b]		13.82 ± 0.2 [b]		13.47 ± 0.20 [b]	

[a] Determined by difference.

[b] Determined from combustion calorimetry.

was determined in two ways: firstly, by subtracting the sum of the percentages of C and H from 100 and, secondly, by combustion calorimetry. The details of the method are described in ref. 4. After the combustion run, the contents in the bomb were washed down and titrated against standardised sodium hydroxide solution. After applying the correction for the presence of N_2 in O_2 gas, the percentages of nitrogen in the compounds were calculated from the resultant HNO_3 estimation. The elemental analyses results are listed in Table 1.

Calorimetric procedures

Combustion calorimetry

In order to obtain heat-of-formation data on the AN–F reaction products, data on the heat of combustion are required. Such data are not available in the literature on these compounds. For the combustion studies (in the presence of 25 atm of O_2) of the reaction products from the reactions using 4 : 1 and 2 : 1 AN/F, a Toshniwal (India) bomb calorimeter was used and for the reaction product from the reaction using 1 : 1 AN/F, a Parr model no. 1243 (Moline, U.S.A.) bomb calorimeter was used. The essential operations of the instruments were carried out as described in the manufacturer's instructions. The calorimetric and calculation procedures adopted were described elsewhere [6]. The energy equivalent of the bomb calorimeters were determined from the combustion of benzoic acid samples (thermochemical grade, Parr, U.S.A.) under standard calorimetric conditions. The values of the energy equivalent of the empty bomb calorimeters were found to be 514.60 ± 0.06 cal°C^{-1} and 452.80 ± 0.02 cal°C^{-1} for the Toshniwal and Parr models, respectively.

TABLE 2

Heat of combustion data of compounds I and II

	Compound I		Compound II	
	Run 1	Run 2	Run 1	Run 2
m, compd (g)	0.27665	0.29280	0.28800	0.27125
m, fuse (g)	0.03400	0.03215	0.03115	0.03330
m, cotton (g)	0.02015	0.02216	0.02320	0.02015
E(cal °C^{-1})	2368.5400	2368.6412	2368.6700	2374.5000
q_N(cal)	3.6135	3.6135	3.6135	3.6135
q_f(cal)	48.7247	46.0735	44.6404	44.7216
q_{cot}(cal)	84.2085	92.6085	96.9547	84.2085
ΔT(corrected) (°C)	1.286	1.358	1.346	1.262
$-\Delta H_c^0$(cal g^{-1})	10562.5900	10546.0950	10566.0460	10547.7430
$-\Delta H_c^0$(kcal mole^{-1})	2091.3928	2088.1268	2092.0771	2088.4531
Mean value	2089.7 ± 1.6		2090.1 ± 1.8	

TABLE 3

Heat of combustion data of the 1 : 1 AN–F resin (in the presence of benzoic acid)

	Run 1	Run 2
m, mixture (g)	0.21745	0.25630
m, C_6H_5COOH (g)	0.13047	0.15378
m, compd. (g)	0.08698	0.10252
m, fuse (g)	0.01264	0.02320
m, cotton (g)	0.02950	0.01370
E(cal °C^{-1})	2255.5000	2251.4000
ΔT(corrected)(°C)	0.757	0.860
q_N(cal)	1.0000	1.0000
q_f(cal)	17.7000	32.4800
q_{cot}(cal)	123.2289	96.9547
Gross heat (cal g^{-1})	7768.9000	7425.6000
Gross heat (cal)	1689.3473	1903.1813
q, C_6H_5COOH (cal)	824.4399	971.7358
$-\Delta H_c^0$, resin (cal g^{-1})	8527.0000	8527.0004
$-\Delta H_c^0$ (kcal mole^{-1})	895.3350	895.3335
Mean value	895.3340 ± 0.0010	

From the trial combustion runs on the 1 : 1 AN–F resinous material, it was found that black residues due to incomplete combustion were left behind. In order to ensure complete combustion, pellets containing a mixture of powdered benzoic acid and the resin mixed in a 3 : 2 ratio by weight, respectively, were used. The heat of combustion due to the incorporated benzoic acid was subtracted from the total heat of combustion to obtain the heat of combustion of the 1 : 1 AN–F resin. Tables 2 and 3 present the ΔH_c^0 data of the reaction products from reactions using 4 : 1, 2 : 1 and 1 : 1 AN/F. The symbols used have the meanings given: m is the mass; E is the energy equivalent of the empty bomb calorimeter plus the water in the bomb and calorimetric bucket; T is the corrected temperature; q_N, q_f and q_{cot} are the energy corrections for the formation of HNO_3, combustion of fuse wire and cotton, respectively.

Solution calorimetry

The exact experimental procedure and a detailed description of the apparatus used are described elsewhere [3]. The general heat balance equation used to calculate the enthalpy of the reaction as mentioned in ref. 3 can be used in the present measurements with certain modifications. This is because, apart from the exothermic nature of the reaction between AN and F, the neutralisation reaction between AN and hydrochloric acid itself exhibits some exothermicity. Correction due to this behaviour, therefore, must be applied to the total heat of reaction in order to estimate the heat of reactions between AN and F alone.

TABLE 4

Heat of neutralisation of aniline and dilute hydrochloric acid

No.	Concn. of HCl	Weight of AN (g)	No. of moles of AN	Vol. of HCl (ml)	ΔT (corrected) (°C)	ΔH_x (cal)	ΔH_N^0(298 K) (kcal per mole of AN)
1	0.9091 N	2.5010	0.0269	87.56	1.476	424.2010	15.7960
2	0.9091 N	3.4805	0.0374	86.60	1.908	548.4132	14.6742
3	0.9091 N	4.5200	0.0485	85.58	2.505	720.0016	14.8349
4	0.9091 N	5.6821	0.0610	84.45	3.021	868.1130	14.2284
5	0.9091 N	7.5208	0.0808	82.65	4.160	1195.6801	14.8601
						Mean	14.8700 ± 0.57

The heats of neutralisation (ΔH_N^0) of AN and HCl acid solution were determined as described. The procedure adopted was the same as described in ref. 3 for the determination of the energy equivalent of the solution calorimeter using the neutralisation reaction of HCl acid and NaOH solu-

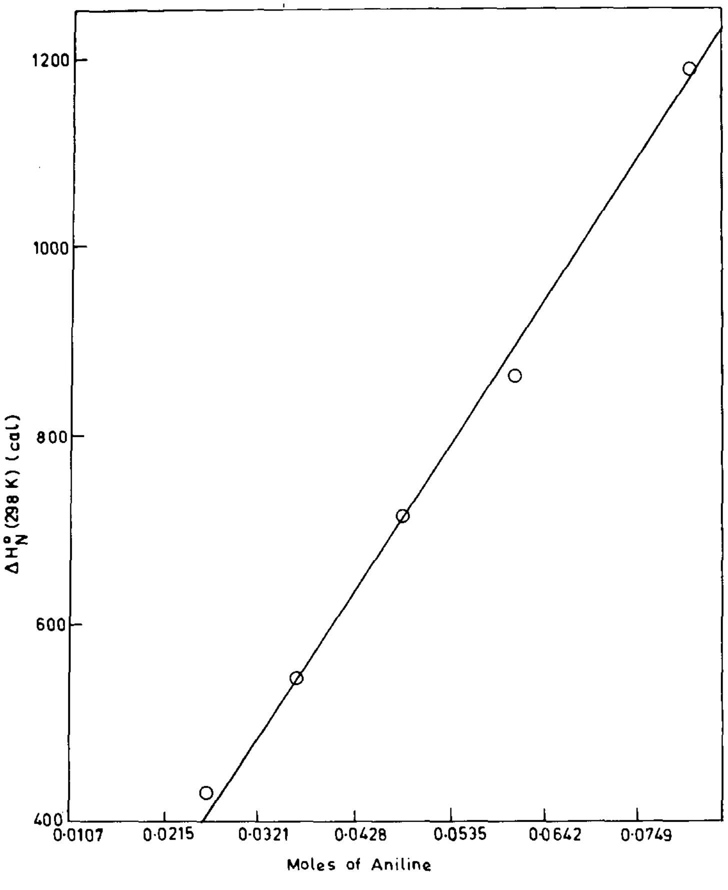


Fig. 1. The plot of heat of neutralisation of AN and HCl vs. the number of moles of AN.

TABLE 5

Heats of reaction of aniline and formaldehyde in acid medium

AN/F ratio	Weight of AN(g)	Corrected weight of F(g)	m_1 (g)	m_5 (g)	ΔT (corrected) (°C)	ΔH_x^0, total enthalpy (k cal)	$\Delta H_x^{0\prime}$ (AN + HCl) (kcal)	ΔH_r^0(298 K) (AN + F) (kcal per mole of AN)	ΔH_r^0(298 K) (AN + F) (kcal per mole of F)
4:1	7.6142	0.6138	80.82	1.570	5.95	1.7100	1.2107	6.1080	24.4330
	8.1044	0.6533	80.22	1.675	6.33	1.8193	1.2886	6.0979	24.3945
							Mean	6.0990 ± 0.0086	24.3971 ± 0.0346
2:1	7.9866	1.2876	78.71	3.30	8.15	2.3423	1.2699	12.5057	25.0133
	7.5941	1.2244	79.27	3.14	7.75	2.2274	1.2075	12.5076	25.0144
							Mean	12.5019 ± 0.0082	25.0040 ± 0.017
1:1	3.8043	1.2267	38.05	3.145	5.375	1.5448	0.6049	23.0089	23.0090
	3.7889	1.2217	38.07	3.135	5.350	1.5376	0.6024	22.9856	22.9855
							Mean	22.9956 ± 0.012	22.9950 ± 0.012

tions. Instead of NaOH solution, weighed amounts of AN were taken in the glass bulb of the solution calorimeter and the volume made up to 90 ml using dil. HCl solution. The concentration of the HCl solution used in all the solution calorimetric runs was 0.9091 N. The energy equivalent of the empty solution calorimeter was determined to be 197.36 ± 0.13 cal $°C^{-1}$. From the corrected temperature rise values, the enthalpy values of complete neutralisation of AN and HCl solution were determined and the results are listed in Table 4. The plot of ΔH_N^0 values vs. the amount of AN taken is shown in Fig. 1. This plot could be used to determine the heat liberated during the neutralisation of AN and HCl acid, if the amount of AN taken is known.

The enthalpies of reaction between 4 : 1, 2 : 1 and 1 : 1 molar proportions of AN and F in the presence of HCl acid are determined as described. The procedure adopted was described in the AN and F reactions carried out in absence of acid catalysts [3]. However, 0.9091 N HCl acid solution was used in place of water. The heat balance equation used to determine the total heats of the reaction was

$$\Delta H_x^0 = \Delta T(w + m_1 + m_5) \tag{1}$$

where ΔH_x^0 is the total heat liberated when x mole of AN was taken; ΔT is the corrected temperature rise; w is the energy equivalent of the empty solution calorimeter; m_1 is the volume of HCl acid solution; m_5 is the sum of the volumes of AN and F and the term m_5 includes the corrected amount of F wherein the loss due to temperature rise has been considered. Since aqueous conditions were maintained, the specific heat of the solution was taken to be 1 cal g^{-1} $°C^{-1}$. In the case of the reaction using 1 : 1 AN–F, after completion of the reaction, if the reactants were left undisturbed, a gel-type material was observed to be formed. Hence, to avoid the recording of the heat change due to gelation, recordings were stopped as soon as the reaction became complete. The ΔH_r^0 values for reactions of AN with F alone were determined using the expression

$$\Delta H_r^0 = \Delta H_x^0 - \Delta H_x^{0'} \tag{2}$$

where $\Delta H_x^{0'}$ is the heat due to the neutralisation of x moles of AN by HCl solution. Table 5 presents the data on each of the typical runs of the reactions using 4 : 1, 2 : 1 and 1 : 1 AN/F molar ratios in the presence of acid

TABLE 6

ΔH_f^0 and ΔH_c^0 data of the reaction products formed by AN + F in acid medium.

Compound	$-\Delta H_c^0$(298 K) (kcal $mole^{-1}$)	ΔH_f^0(298 K) (kcal $mole^{-1}$)
I	2089.7 ± 1.6	19.58 ± 0.05
II	2090.1 ± 1.8	19.70 ± 0.05
III	895.334 ± 0.001	18.06 ± 0.03

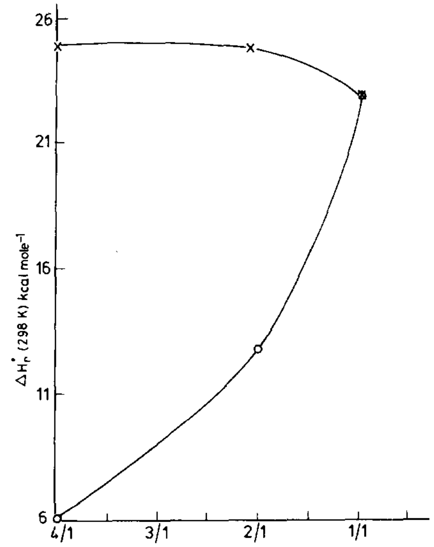


Fig. 2. Dependence of ΔH_r^0 of the AN–F reaction in acid medium at different AN/F ratios. ΔH_r^0(kcal mole^{-1}) for ×, F and ○, AN.

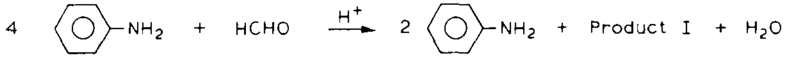
medium. Figure 2 shows the plot of ΔH_r^0 of the reactions of AN with F calculated separately with respect to per mole of AN and per mole of F vs. different molar ratios of AN and F.

RESULTS AND DISCUSSION

The reactions using 4 : 1 and 2 : 1 AN/F fall in the category of reactions of AN with F in an excess of AN. In the reaction using 2 : 1 AN/F no residual AN or F was found to remain unreacted. In the reaction using 4 : 1 AN/F, half of the initial amount of AN was left unreacted: this was later removed by steam distillation. For convenience, let the solid products obtained from the reactions using 4 : 1, 2 : 1 and 1 : 1 AN/F be designated as I, II and III, respectively. Table 2 shows that the ΔH_c^0 values of I and II coincide. The ΔH_r^0 values (Table 5) of the reactions using 4 : 1 and 2 : 1 AN/F calculated with respect to per mole of F are the same. Also, compounds I and II possess identical melting points (91.0 ± 0.05°C) and identical R_f values. From these results it may be said that compounds I and II are the same.

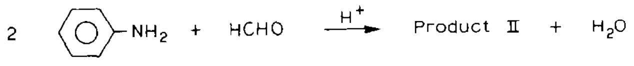
The thermochemical approach using the ΔH_f^0 and ΔH_r^0 values to ascertain the structure of the products was adopted as described. The molecular formula of compounds I and II were derived by balancing the number of C, H, N and O atoms of reactants and products in the respective equations as given.

For the reactions using 4 : 1 AN/F


(3)

The molecular formula of I is, therefore equal to $C_{13}H_{14}N_2$ for the reaction $C_{24}H_{28}N_4 + CH_2O \rightarrow C_{12}H_{14}N_2 - H_2O$.

Similarly, for the following reaction using 2 : 1 AN/F

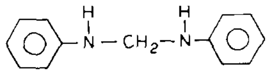
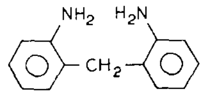
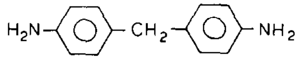
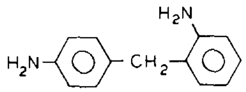
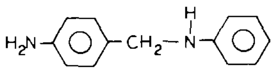
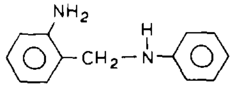

(4)

the molecular formula of II is, therefore, equal to $C_{13}H_{14}N_2$.

It may be clearly seen that compounds I and II possess the same molecular formula. The elemental analysis data obtained both by calculation from the molecular formula and by experimental methods (Table 1) seem to agree well. The percentage weight of nitrogen obtained from bomb calorime-

TABLE 7

Data on heats of formation of some aniline–formaldehyde reaction products

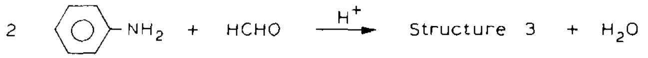
No.	Structure	M.Pt. (°C)		ΔH_f^0 (298 K) from Benson's thermochemical method (kcal mole^{-1})	ΔH_r^0 (298 K) from Benson's ΔH_f^0 values (kcal mole^{-1})
		Exptl.	Literature		
1			65	36.24 ± 0.05	− 10.860 ± 0.05
2			158	20.64 ± 0.05	− 26.46 ± 0.05
3		91 ± 0.05	92		
4			88		
5				25.84 ± 0.05	− 21.250 ± 0.05
6					

try also showed a good agreement with the calculated value (Table 1). The ΔH_f^0 values of compounds I and II were calculated from the ΔH_c^0 values and are listed in Table 6. The ΔH_f^0 values of compounds I and II are the same.

Among the numerous possible structures written in concurrence with the molecular formula $C_{13}H_{14}N_2$, only those structures which would be the possible products of reactions between AN and F in that desired stoichiometric reaction are listed in Table 7. In order to choose one among the various possible structures of compounds and I and II, the ΔH_f^0 values of structures 1 to 6 have been calculated using Benson's method of thermochemical calculations [7]. Table 7 presents the calculated ΔH_f^0 values of structures 1 to 6. On comparing the results presented in Tables 5 and 7 i.e. values obtained experimentally and theoretically respectively, it may be inferred that the ΔH_f^0 value calculated for structure 3 agrees well with the experimentally determined ΔH_f^0 value of compounds I and II. Thus, it is obvious that 4,4′-diaminodiphenylmethane, i.e. structure 3, corresponds to the structure of compounds I and II.

In addition to the ΔH_f^0 values, analysis of ΔH_r^0 values obtained experimentally were undertaken for further confirmation. Assuming each of the structures 1 to 6 to be the sole solid product in each of the reactions using 4 : 1 and 2 : 1 AN/F, the ΔH_r^0 values were calculated using the calculated ΔH_f^0 values of reactants and products. A calculation is given to illustrate this method.

For the reaction using 2 : 1 AN/F



(5)

$$\begin{aligned}\Delta H_r^0(298\ \mathrm{K}) &= \Delta H_f^0\,[\text{structure 3}] + \Delta H_f^0[H_2O] - 2\Delta H_f^0[\mathrm{AN}] - \Delta H_f^0[\mathrm{F}]\\ &= 20.640 - 68.315 - 2 \times 7.34 + 35.90\\ &= -26.40 \pm 0.05 \text{ kcal per mole of F}\end{aligned}$$

$$\Delta H_r^0 \text{ (observed)} = -25.004 \pm 0.017 \text{ kcal per mole of F}$$

Thus, ΔH_r^0 values calculated in the same way for each of the structures 1 to 6 are listed in Table 7. It may be seen from the ΔH_r^0 values in Tables 7 and 5 that the calculated and experimental ΔH_r^0 values for structure 3 are in good agreement, thereby confirming the inference made earlier on the basis of ΔH_f^0 values alone.

Spectral analysis of compounds I and II have been undertaken in order to further verify the thermochemical inferences. Figures 3 and 4 present the IR and NMR spectra, respectively, of compound II. The IR and NMR spectra of compounds I and II were found to be the same. The IR spectrum contains two strong bands around 3400–3500 cm^{-1} and a medium band around 1650–1600 cm^{-1} corresponding to the stretching and bending modes, respectively, of vibration of primary amino N–H bonds. A strong band around

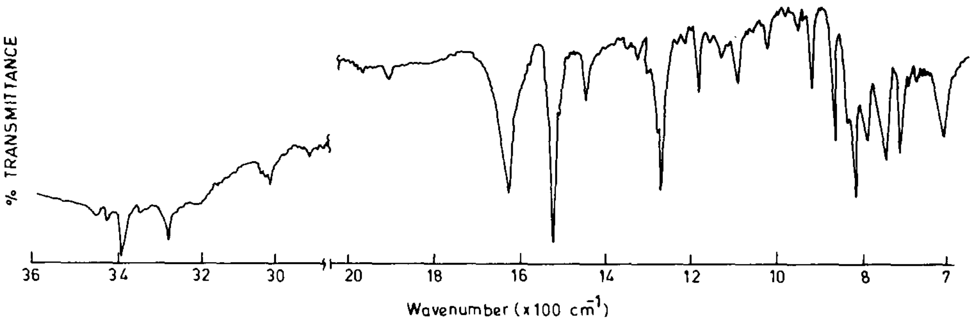


Fig. 3. IR spectra of compound II in KBr pellet.

1340–1250 cm^{-1} corresponds to the aromatic C–N primary vibrations. A medium band around 830 cm^{-1} corresponds to the absorption of two adjacent hydrogens in the phenyl ring (i.e. a *p*-disubstituted phenyl ring), while other bands correspond to skeletal vibrations of aromatic rings. However, there is no evidence for the free O–H or secondary N–H groupings to be seen in the IR spectra.

In the H^1 NMR spectra (Fig. 4) taken in $CDCl_3$ solvent, a quartet at 7.0δ, a singlet at 3.75δ and a singlet at 3.25δ, corresponding to the hydrogens attached to phenyl ring, methylene carbon and nitrogen, respectively, are seen. The intensity of these peaks were found to be in the ratio of 4 : 1 : 2 which could be possible only in the case of structure 3. It is clear that the thermochemical data support for structure 3 has been validated by the spectral data.

In the reaction using 1 : 1 AN/F molar ratio conducted in the presence of

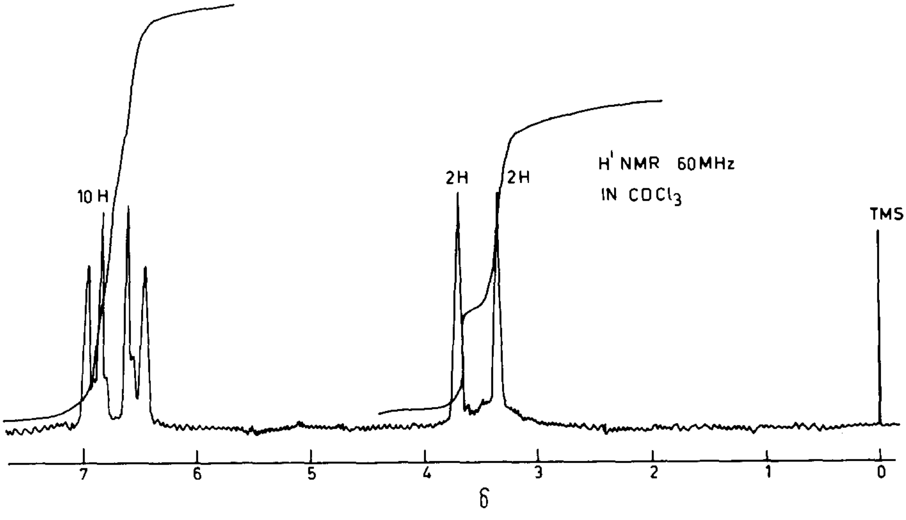
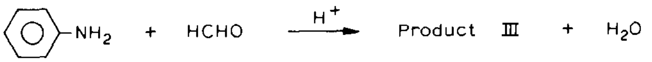


Fig. 4. H^1 NMR spectrum of compounds I and II.

acid catalysts, no excess of unreacted AN of F was detected. However, the solid product recovered was entirely different from the products from the reactions using 4 : 1 and 2 : 1 AN/F and exhibited hard, infusible, insoluble resinous behaviour. Since there is complete reaction between AN and F in the reaction using a 1 : 1 molar ratio, the molecular formula of the solid product III, could be derived by balancing the total number of C, H, N and O atoms of the reactants and products.



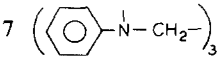
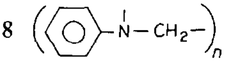
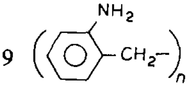
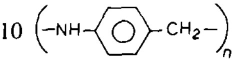
(6)

The molecular formula of III in eqn. (6) is derived to be C_7H_7N. The elemental analysis values calculated from the molecular formula C_7H_7N for compound III are found to be in good agreement with that obtained experimentally (Table 1). Also, the estimation of N from combustion calorimetry shows an agreement with the theoretical value calculated from the molecular formula and from the difference method (Table 1). The ΔH_f^0 value of the 1 : 1 AN–F resin as given in Table 6 was calculated from the ΔH_c^0 value using the derived molecular formula (C_7H_7N).

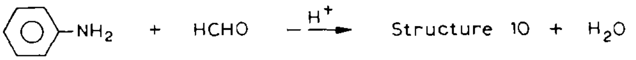
The possible structures derived for the same molecular formula (C_7H_7N) which could be formed in the reaction using 1 : 1 AN/F are listed in Table 8. In order to confirm one among the possible structures, the ΔH_f^0 values were calculated for structures 7 to 10 using Benson's thermochemical calculations [7] and the respective calculated values are listed in Table 8. Upon compar-

TABLE 8

Data on ΔH_r^0 and ΔH_f^0 values of the reaction using 1 : 1 AN/F and the products

No.	Structure	M.Pt(°C) Exptl.	M.Pt(°C) Literature	ΔH_f^0 (298 K) from Benson's thermochemical method (kcal mole^{-1})	ΔH_r^0 (298 K) from Benson's ΔH_f^0 values (kcal per mole of AN or F)
7		141 ± 0.05	141	80.07 ± 0.05	− 13.065 ± 0.05
8				36.19 ± 0.05 (kcal per mole of monomer)	− 3.605 ± 0.05
9				3.34 ± 0.05	− 27.415 ± 0.05
10				18.92 ± 0.05	− 20.835 ± 0.05

ing the experimentally determined and theoretically calculated ΔH_{f}^0 values, i.e. Tables 6 and 8, it is clear that structure 10 exhibits a good agreement. As a further experimental confirmation the ΔH_{r}^0 values of the reaction using 1 : 1 AN/F were calculated theoretically using the calculated ΔH_{f}^0 value of each of the structures from 7 to 10: the corresponding values are listed in Table 8. From the ΔH_{r}^0 values listed in Tables 5 and 8, it is seen that structure 10 shows agreement between the experimental and theoretically calculated ΔH_{r}^0 values for the reaction using 1 : 1 AN/F. That is, for the reaction using 1 : 1 AN/F



$$C_6H_5NH_2 + HCHO \xrightarrow{H^+} \text{Structure 10} + H_2O \qquad (7)$$

$$\begin{aligned}\Delta H_{\mathrm{r}}^0(298\ \mathrm{K}) &= \Delta H_{\mathrm{f}}^0[\text{structure } 10] + \Delta H_{\mathrm{f}}^0[\mathrm{H_2O}] - \Delta H_f^0(\mathrm{AN}) - \Delta H_{\mathrm{f}}^0(\mathrm{F})\\ &= 18.92 - 68.315 - 7.34 + 35.9\\ &= 20.835 \pm 0.05\ \text{kcal mole}^{-1}\end{aligned}$$

$$\Delta H_r^0(\text{observed}) = 22.995 \pm 0.012\ \text{kcal per mole of AN or F}$$

However, in order to conclude the chemical structure derived from the thermochemical calculations, spectral analysis of the 1 : 1 AN/F resin was undertaken. Since the resin was practically insoluble in organic solvents, H^1 NMR spectra could not be taken. Figure 5 presents the IR spectra of the powdered resin taken in KBr pellets. The IR spectra contain only a few broad bands since these resinous compounds belong to high polymeric materials [8]. Only strong and principal bands are visible. Strong bands around 3400 cm^{-1} and 2500–3000 cm^{-1} correspond to secondary amino group and $-CH_2-$ group stretching, respectively. The band around 1650 cm^{-1} contains overlapping of secondary N–H and $-CH_2-$ bending and bands around 1600–1450 cm^{-1} correspond to aromatic ring vibrations. A band around 830 cm^{-1} corresponds to *p*-disubstituted phenyl ring –C–H vibrations. A single weak band around 1350 cm^{-1} corresponds to C–N bond

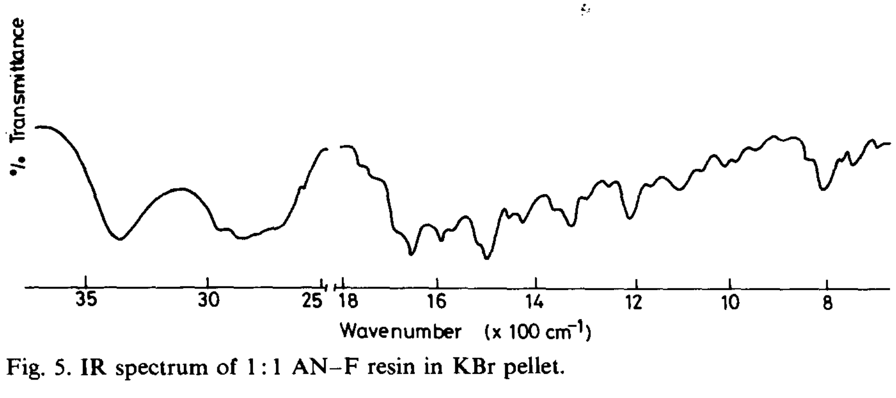
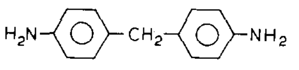
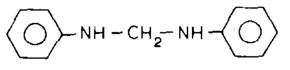


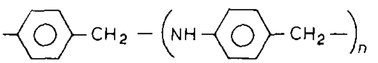
Fig. 5. IR spectrum of 1 : 1 AN–F resin in KBr pellet.

TABLE 9

Thermochemical data on aniline–formaldehyde reactions in the presence and absence of acid catalyst

	4 : 1 AN/F	
	In presence of H^+	In absence of H^+
ΔH_r^0(kcal per mole of F)	24.39 ± 0.04	21.1930 ± 0.002
Structure of product	 4, 4'-diaminodiphenyl-methane (DADPM)	 dianilinodiethane (DAM)
ΔH_f^0 of product (kcal $mole^{-1}$)	19.58 ± 0.05	34.75 ± 0.15
ΔH_c^0 of product (kcal $mole^{-1}$)	2089.7 ± 1.6	1694.9 ± 5.3

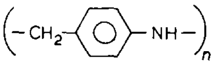
vibrations. The absence of primary and tertiary nitrogen of the amino group confirms a linear structure. The stoichiometric, thermochemical and spectral data lead us to write the following linear structure for the 1 : 1 AN/F resin, i.e.



Frey [9] investigated the AN–F resinous material from the reaction using 1 : 1 AN/F based on classical chemical analytical methods (viz. reduction studies) and speculated a polymeric structure equivalent to structure 10 of compound III. He also obtained an identical resin when *p*-amino benzyl alcohol was treated with acids. from the foregoing discussion it is, therefore, clear that a linear polymeric structure exists for the product from the reaction using 1 : 1 AN/F. Due to the insoluble nature, molecular weight determination and other spectral analyses of the resin were rendered infeasible.

Comparative study of reactions in non-acid and acid media

A distinct comparative study can now be made on the AN and F reactions conducted in the presence and absence of acid catalysts based mainly on the thermochemical observations reported both in the past [3,4] and in the present investigation. Table 9 presents the ΔH_r^0 results and structures of the reaction products obtained from the reactions using 4 : 1, 2 : 1 and 1 : 1 AN/F molar ratios carried out in the presence and absence of acid medium. The ΔH_r^0 values of the reaction using 4 : 1 AN/F calculated with respect to

2 : 1 AN/F		1 : 1 AN/F	
In presence of H^+	In absence of H^+	In presence of H^+	In absence of H^+
25.004 ± 0.020	21.190 ± 0.004	22.99 ± 0.01	13.750 ± 0.003
DADPM	DAM		Anhydro-formaldehyde aniline
19.70 ± 0.05	34.99 ± 0.15	18.06 ± 0.03	84.30 ± 0.15
2090.1 ± 1.8	1695.2 ± 8.5	895.33 ± 0.001	2715.6 ± 10.5

per mole of F coincide with the ΔH_r^0 value of the reaction using 2 : 1 AN/F calculated with respect to per mole of F for both in the presence and absence of acid catalysts. That is, the limiting factor for the reactions in excess moles of AN with F is two, either in acid or in non-acid medium. This requirement that AN be two during condensation reactions has also been reported elsewhere [1]. From Fig. 2 and Table 5 it is also clear that the ΔH_r^0 values calculated with respect to per mole of F are the same for the reactions using 4 : 1 and 2 : 1 AN/F molar ratios indicating that even in the presence of more than 2 moles of AN, one mole of formaldehyde can consume only two moles of AN. Also, the ΔH_r^0 values of the reactions using 4 : 1, 2 : 1 and 1 : 1 AN/F carried out in the presence of acids are higher than the ΔH_r^0 values of the corresponding reactions carried out in absence of acid medium (Table 9). This observation clearly indicates that the reaction products obtained from the AN/F reactions in the presence of acids are more stable than the reaction products obtained in the absence of acid catalysts. If one considers the structures of the reaction products obtained, i.e. *N*,*N*′-methylenebisaniline and 4,4′-diaminodiphenylmethane, from the reaction using 2 : 1 AN/F carried out in the absence and presence of acid medium, respectively, the two compounds are seen to be isomeric in nature. However, the bonding of the $-CH_2-$ linkage occurs at the nitrogen of the amino group in the former structure while the $-CH_2-$ linkage occurs at the *para* carbon atom of the phenyl ring in the latter structure. That is, only low molecular weight methylene phenylene bases are obtained when excess moles of AN are reacted with F under acidic as well as non-acidic conditions.

In the case of the reactions using 1 : 1 AN/F, the ΔH_r^0 values of the reactions conducted in the presence of acid catalysts are nearly one and half times that of the ΔH_r^0 values of reactions carried out in the absence of acid catalysts (Table 9). This may be because of the polymeric nature of the product obtained in the reaction using 1 : 1 AN/F carried out in the presence of an acid catalyst. That is, only a trimeric Schiff's base (i.e. anhydroformaldehyde aniline) has been obtained in non-acidic conditions while a polymeric Schiff's base (i.e. poly-anhydro-*p*-aminobenzylalcohol) has been obtained in acidic conditions. Also, the structural and physical properties of the two compounds are entirely different. Due to the hard, insoluble and infusible nature of the 1 : 1 AN–F resin, it has been used in industrial applications. Here, one may also see that, the polymeric structure has resulted from the bonding of the $-CH_2-$ linkage between the N of the amino group of one aniline molecule and the *para* carbon of the phenyl ring of the other aniline molecule. This change in the attack of the $-CH_2-$ grouping has been brought about by the presence of H^+ species. This difference in the types of bond formation, i.e. between $-\overset{|}{N}-CH_2-$, $-\overset{|}{N}-CH_2-\underset{|}{\overset{|}{C}}-$ and $-CH_2-\underset{|}{\overset{|}{C}}-$, are well reflected in the change in the ΔH_r^0 values of AN/F reactions with the same stoichiometry when carried out in the presence and absence of acid catalysts. This information obtained from the thermochemical data agrees quite well with that obtained by other workers adopting different methods of analysis. Thus, thermochemical methods of analysis could be used in the case of reactions yielding high polymeric thermoset materials to obtain equally valid information as that obtained from other techniques to which these materials could not be subjected.

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