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A THERMOCHEMICAL KINETIC STUDY OF INTERCONVERSION REACTIONS OF ANILINE–FORMALDEHYDE PRODUCTS

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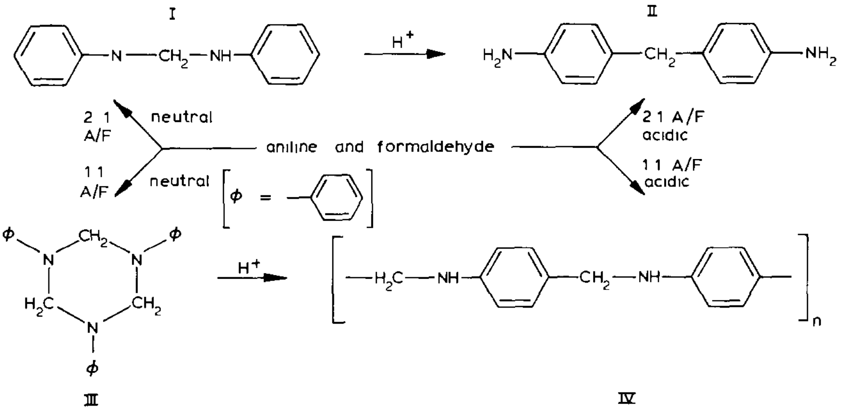
ABSTRACT

$\Delta H_r^{\ominus}$ and rate constant values of the conversion reactions of dianilinomethane to 4,4′-diaminodiphenylmethane and 1,3,5-triphenylhexahydro-*s*-triazine to polyanhydro-*p*-aminobenzyl alcohol in acid medium are determined adopting solution calorimetry and kinetic methods, respectively The mechanistic aspects of the reactions are rationalized collating experimental and theoretical thermochemical kinetic data

INTRODUCTION

A thermochemical rationalization of aniline (A) and formaldehyde (F) reactions and the products at varying stoichiometries of reactants in presence and absence of the acid catalyst have been reported earlier [1–4] A 2 1 A/F mole ratio reaction produces exclusively dianilinomethane (I) and 4,4′-diaminodiphenylmethane (II) in the absence and presence of acid medium, respectively, while in 1 1 A/F stoichiometric reaction, 1,3,5-triphenylhexahydro-*s*-triazine (III) and polyanhydro-*p*-aminobenzylalcohol (IV) (a polymer) are the products in absence and presence of acid medium,



(1)

(2)

respectively It is observed that I and III self converted to II and IV, respectively, when dissolved in acid solutions

Literature shows that investigations on the interconversion reactions (1) and (2) are not available so far and, therefore, in the present report mechanistic analyses of reactions (1) and (2) have been attempted via a thermochemical and kinetic approach

EXPERIMENTAL

Compounds I and III are prepared in the laboratory from 2 1 and 1 1 A/F reactions conducted in neutral medium [1,2] and are twice recrystallized from CCl_4 solvent [m p I, 61 ± 0 2°C, II, 141 ± 0 2°C] Concentrated HCl (BDH, analar grade) and triple-distilled water used to prepare acid solutions.

Apparatus and the $\Delta H_r^\ominus$ data evaluations are the same as mentioned elsewhere [1] except that compounds I and II have been used in lieu of A and dilute HCl solution in lieu of F Table 1 summarizes $\Delta H_r^\ominus$ values obtained for reactions (1) and (2) For kinetic measurements, each of the thermochemical experimental runs has been identically duplicated in a thermostatted bath of 25 ° C Since in each kinetic run the ΔT did not exceed two degrees, the kinetic parameters correspond to 25 ° C in all cases After the inception of reaction, exactly 10-ml aliquots are drawn out at regular intervals of time and reaction progress is arrested by adding an equal volume of equally concentrated NaOH solution The solid separated out containing unreacted I and II was filtered, dried and weighed Since com-

TABLE 1

Data on enthalpy of conversion reactions of I and III

Weight of substrate (g)	Weight of 0 1 N HCl (g)	ΔT (° C)	$\Delta H_x^\ominus$ [a] (kcal)	$\Delta H_r^\ominus$ (298 K) (kcal mol^{-1}) [b]	(ΔT) (corrected) (° C)	$\Delta H_r^\ominus$ (corrected) (298° K) (kcal mol^{-1})
(1) Dianilinomethane to 4,4′-diaminodiphenylmethane						
7 5012	90 0000	1 84	0 5425	14 3193	1 85	14 4073
6 5323	91 1555	1 60	0 4713	14 2849	1 61	14 4218
5 2114	92 7886	1 28	0 3777	14 3493	1 29	14 4144
(2) 1,3,5-Triphenylhexahydro-*s*-triazine to polyanhydro-*p*-aminobenzylalcohol						
6 5007	91 3215	0 62	0 1832	8 8781	0 625	8 9018
6 7373	91 1500	0 64	0 1888	8 8264	0 645	8 9147
5 3750	92 5274	0 51	0 1511	8 8543	0 515	8 8996

[a] The water equivalent of the calorimeter is 197 36 cal ° C^{-1}

[b] Mean for reaction (1), 14 4145 ± 0 0103 kcal mol^{-1}, mean for reaction (2), 8 9054 ± 0 0100 kcal mol^{-1}

TABLE 2

Kinetic data on conversion reactions of I and III

[Substance] (mol dm^{-3})	[H$^+$] (mol dm^{-3})	Rate constants $\times 10^4$ (s^{-1})
(1) I to II		
0 1	0 1	1 05 ± 0 02
0 1	0 3	3 18 ± 0 04
0 2	0 1	2 19 ± 0 01
0 5	0 1	5 31 ± 0 03
(2) III to IV		
0 1	0 1	2 5 ± 0 03
0 1	0 5	12 8 ± 0 02
0 2	0 1	5 1 ± 0 03
0 5	0 1	12 7 ± 0 04

pounds I and II dissolve in C_6H_6 solvent, the TLC technique was employed to remove I from II [R_f of I = 0 98, R_f of II = 0 61] Thus, the amount of II obtained from each aliquot is determined and a plot of amount converted versus time is made for the evaluation of kinetic parameters

In reaction (2) product IV is a thermosetting insoluble polymer, which separates out after the neutralization of each aliquot with NaOH solution When C_6H_6 solvent only was added, III dissolved leaving behind the polymeric product From the plots of amount converted versus time, rate constants and orders of reactions (1) and (2) are determined by available methods [5,6] The kinetic data obtained are presented in Table 2 Despite the adiabatic conditions maintained in a thermochemical run, changes in $\Delta H_r^{\ominus}$ values due to changes in T and rate as the reaction proceeds, should

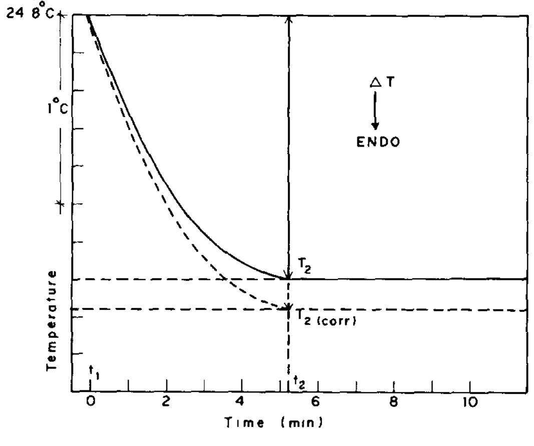


Fig 1 A typical time–temperature plot The broken curve shows the corrected plot

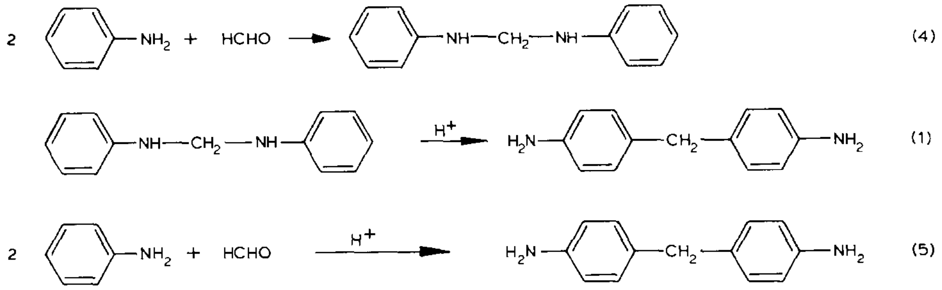
be corrected Using the rate values, corrected ΔT vs Δt plots are reconstructed (Fig 1) as follows

$$\text{correct } \Delta H_r^{\ominus} = \text{observed } \Delta H_r^{\ominus} + \frac{\Delta x}{\Delta t} \Delta t C_p (\Delta T)_{\Delta t} \frac{M}{\Delta x} \frac{1}{1000} \qquad (3)$$

where $\Delta H_r^{\ominus}$ is the heat of reaction in kcal mol^{-1}, $\Delta x/\Delta t$ is the rate in gs^{-1}, C_p is the specific heat of production in cal g^{-1} °C and M is the molecular weight of the product in g The unit of all the terms in eqn (3) is kcal mol^{-1} From corrected $\Delta H_r^{\ominus}$ values corrected ΔT values could be determined corresponding to each time interval

RESULTS AND DISCUSSION

Table 3 furnishes $\Delta H_r^{\ominus}$ values of 2 1 and 1 1 A/F stoichiometric reactions conducted in acid and neutral medium [1,2] The total enthalpy change incurred during reaction (1) can be derived by combining the $\Delta H_r^{\ominus}$ values of 2 1 A/F reactions in Table 3 in the following way



Subtraction of $\Delta H_r^{\ominus}$ of (1) from $\Delta H_r^{\ominus}$ of (4) results in $\Delta H_r^{\ominus}$ of (5) $\Delta H_r^{\ominus}$ of (4) and $\Delta H_r^{\ominus}$ of (5) are known from Table 3 Thus, $\Delta H_r^{\ominus}$ of reaction (1) is determined to be +14 4 kcal mol^{-1}, which agrees with $\Delta H_r^{\ominus}$ of intercon-

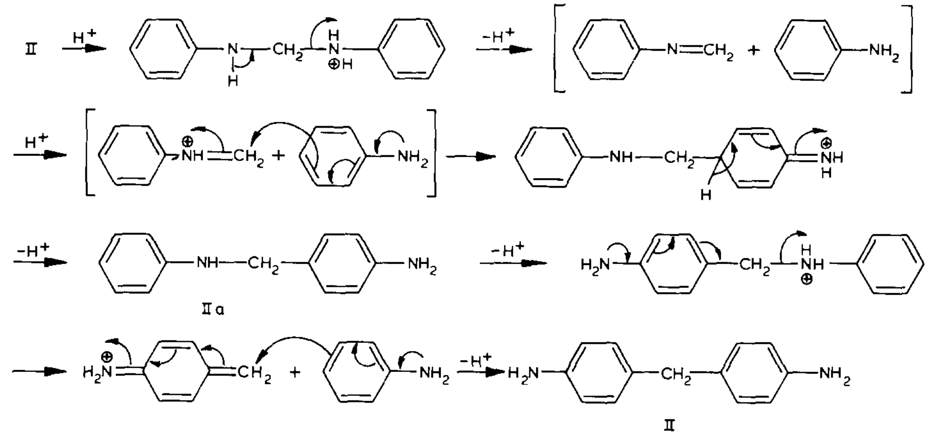
TABLE 3

Heats of reaction data on A–F reactions

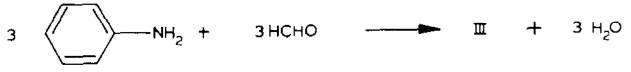
A/F ratio	$-\Delta H_r^{\ominus}$ (298 K) [a] (kcal (mol A)$^{-1}$)	$-\Delta H_r^{\ominus}$ (298 K) [a] (kcal (mol F)$^{-1}$)
Neutral medium		
2 1	5 3	10 6
1 1	13 8	13 8
Acidic medium		
2 1	12 5	25 0
1 1	23 0	23 0

[a] All $\Delta H_r^{\ominus}$ values are within ±0 05 kcal mol^{-1} error

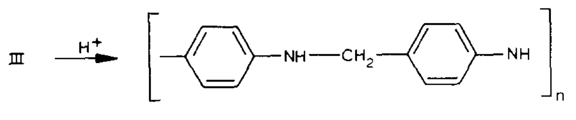
version of I to II found in the present work (Table 1), i.e. the conversion of I to II involves an endothermic process while the formation reactions of I and II from A and F are exothermic in nature. Under excess H^+ the reaction follows a first order course with respect to I and, since the formation of *N*-phenyl-*p*-aminobenzylamine (II_a) has been reported earlier by others [7], and also since the heat changes involving the protonation steps are equally nullified by the heat changes involving the deprotonation steps, a schematic conversion of I to II can be written as



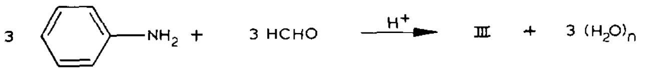
The total enthalpy change of the above reaction course would then be due to net heat changes incurred in two C(H_2)–N bond dissociations, two C_B–C bond formations (where C_B refers a benzene carbon), two (H)N–H bond formations and two C_B–H bond dissociations. Using the bond energy values reported in the literature [8–10] and adopting the computational methods involved in their determination steps [2,3], $\Delta H_r^{\ominus}$ is found to $+13.9 \pm 0.1$ kcal mol^{-1}, which agrees fairly well with the empirical value



(6)



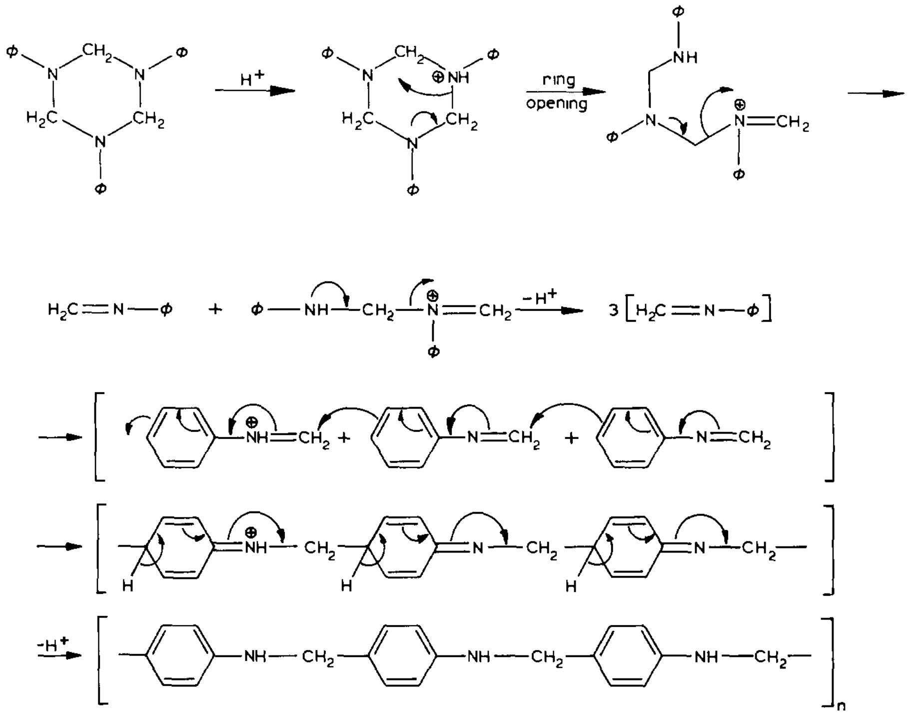
(2)



(7)

Similarly, the $\Delta H_r^{\ominus}$ value of reaction (2) involving conversion of III to IV can be derived by subtracting $\Delta H_r^{\ominus}$ of (7) from $\Delta H_r^{\ominus}$ of (6) using Table 3 values. In doing so, $\Delta H_r^{\ominus}$ of reaction (2) is found to be $+9.2$ kcal mol^{-1}

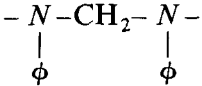
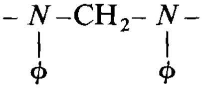
Despite the formation reactions of III and IV from A and F being exothermic in nature, conversion reaction of III to IV is endothermic in nature Also, since *N*-methylene aniline, which is an unstable intermediate formed in all reactions of A and F, immediately polymerize analogous to vinyl monomers, the most plausible interconversion scheme of III to IV in presence of H^+ could be written as



IV

The total enthalpy change incurred during the transformation of III to IV may be taken as due to enthalpy changes involved in three $(H_2)C\text{–}N(C_B)$ bond dissociations and two $(H_2)C\text{–}C_B$ bond formations Applying the reported bond energy values [8–10], the net enthalpy change is calculated to be $+8\ 9 \pm 0\ 1$ kcal mol^{-1} which agrees well with the experimental value This would be so only if the above schemes are operative

Instead of a stepwise conversion of I to II, an intramolecular rearrangement of I similar to homobenzidine rearrangement differing only by a methylene bridge between two N atoms could also be considered Also, apart from II, formations of *o,o′* and *o,p′*-isomers of II are possible But theoretical computations of $\Delta H_r^{\ominus}$ values of reactions involving these isomers produce offset values of $\Delta H_r^{\ominus}$ from the experimental values, thus showing their absence in reaction (1) However, investigations on the cross-over techniques on the molecular fragmentation mechanism are still in progress

In the case of reaction (2), it seems unlikely that a linear polymer of the type  $-\underset{\substack{|\\ \phi}}{N}-CH_2-\underset{\substack{|\\ \phi}}{N}-$ would definitely exist since in presence of H^+ the *para* position of the anilinium ion is more activated so that the methylene carbon links at the *para* position instead of forming a  $-\underset{\substack{|\\ \phi}}{N}-CH_2-\underset{\substack{|\\ \phi}}{N}-$ network

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