

Neighbouring group participation in the gas-phase pyrolysis kinetics of 4-(*N*-methyl-*N*-phenylamino)-1-butyl acetate and 4-(*N*-phenylamino)-1-butyl acetate

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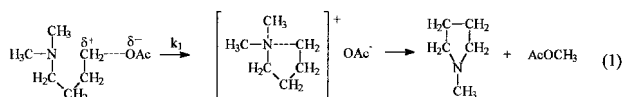
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ABSTRACT: The pyrolysis kinetics of two phenylaminobutyl acetates were determined in a static system over the temperature range 359.7–399.6 °C and the pressure range 23.8–95 Torr. The reactions, in vessels seasoned with allyl bromide and in the presence of the free radical inhibitor toluene, are homogeneous and unimolecular, and obey a first-order rate law. The overall rate coefficients are expressed by the following equations: for 4-(*N*-methyl-*N*-phenylamino)-1-butyl acetate, $\log[k_1 (\text{s}^{-1})] = (13.92 \pm 0.36) - (210.4 \pm 4.5) \text{ kJ mol}^{-1} (2.303RT)^{-1}$; and for 4-(*N*-phenylamino)-1-butyl acetate, $\log[k_1 (\text{s}^{-1})] = (12.03 \pm 0.43) - (188.3 \pm 5.3) \text{ kJ mol}^{-1} (2.303RT)^{-1}$. The decomposition of these substrates undergoes a parallel reaction. The predominant primary product, the corresponding heterocyclic product, appears to be the result of an anchimeric assistance of the amino substituent for a back-side displacement. This suggests that an incipient ion-pair type of mechanism may be operating during the process of elimination. The Arrhenius expressions for the parallel decomposition of each of the aminobutyl acetate substrates are presented and discussed. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: phenylaminobutyl acetates; gas-phase pyrolysis kinetics; neighbouring group participation

INTRODUCTION

Few reactions involving neighboring group participation in true gas-phase experiments have been reported.^{1–4} In this respect, an unusual homogeneous, unimolecular back-side displacement of an ester in the gas phase has been described in the pyrolysis kinetics of 4-(*N,N*-dimethylamino)-1-butyl acetate.⁵ This amino ester was found to give *N*-methylpyrrolidine and methyl acetate. In this respect, the result suggested that the (CH₃)₂N group provided an anchimeric assistance in the elimination reaction. The mechanism was explained in terms of a modest intimate ion-pair type of intermediate, where the acetoxyl leaving group proceeds by an intramolecular solvation or autosolvation to abstract a CH₃ from (CH₃)₂N to give the products as described in reaction (1).



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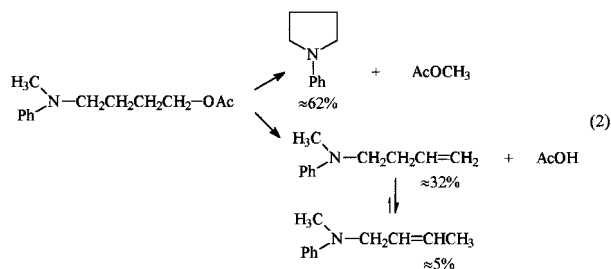
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In view of the scarce literature reports of true gas-phase *trans*-eliminations of carboxylic esters, the present work was aimed at examining the extent to which the presence of a phenyl group at the nitrogen atom may affect the participation of the amino group in the gas-phase elimination reactions of Ph(CH₃)NCH₂CH₂CH₂CH₂OAc and PhNHCH₂CH₂CH₂CH₂OAc.

RESULTS AND DISCUSSION

4-(*N*-Methyl-*N*-phenylamino)-1-butyl acetate

The pyrolysis products of 4-(*N*-methyl-*N*-phenylamino)-1-butyl acetate described in reaction (2) require a twofold



increase in the final pressure, P_f , i.e. $P_f/P_0 = 2.0$. The

Table 1. Stoichiometry of the reactions

<i>4-(N-Methyl-N-phenylamino)-1-butyl acetate at 370.1 °C:</i>					
Time (min)	8	12	16	20	
Reaction (%) (pressure)	28.8	39.0	49.4	59.3	
<i>N</i> -Phenylpyrrolidine (%) (GLC)	17.9	24.3	30.7	36.9	
Acetic acid (%) (titration)	10.9	14.6	17.9	21.5	
<i>4-(N-Phenylamino)-1-butyl acetate at 389.5 °C:</i>					
Time (min)	2	3	6	8	10
Reaction (%) (pressure)	15.5	24.8	43.4	51.2	58.9
Acetic acid (%) (titration)	16.0	25.1	44.4	50.9	55.9

Table 2. Homogeneity of the reactions

Compound	S/V (cm ⁻¹) ^a	$10^4 k_1$ (s ⁻¹) ^b	$10^4 k_1$ (s ⁻¹) ^c
<i>4-(N-Methyl-N-phenylamino)-1-butyl acetate at 389.5 °C</i>	1	21.33	20.85
	6	20.75	21.00
<i>4-(N-Phenylamino)-1-butyl acetate at 389.6 °C</i>	1	19.70	15.33
	6	22.64	15.10

^a S = surface area; V = volume.^bClean Pyrex vessel.^cVessel seasoned with allyl bromide.**Table 3.** Effect of the inhibitor toluene on rates^a

Substrate	P_0 (Torr)	P_i (Torr)	P_i/P_0	$10^4 k_1$ (s ⁻¹)
<i>4-(N-Methyl-N-phenylamino)-1-butyl acetate at 370.1 °C</i>	38.5	—	—	7.95
	70	66	0.9	7.24
	59	157.5	2.7	6.92
	40.5	127	3.1	6.95
<i>4-(N-Phenylamino)-1-butyl acetate at 370.1 °C</i>	71	—	—	5.61
	58.6	33.4	1.8	5.43
	87.5	34.5	2.5	5.41
	152.6	32.4	4.7	5.57

^a P_0 = pressure of the substrate; P_i = pressure of toluene inhibitor. Vessel seasoned with allyl bromide.

average experimental result for P_i/P_0 at four different temperatures and 10 half-lives is 2.09. An additional confirmation of the stoichiometry of reaction (2), up to 60% decomposition, was obtained by comparing the pressure measurements with the sum of the quantitative gas chromatographic analysis of *N*-phenylpyrrolidine and titration of acetic acid with 0.05 M NaOH solution (Table 1).

The pyrolytic elimination of reaction (2) is homogeneous since no significant variations in the rates are observed in these experiments when using both clean Pyrex and seasoned vessels with a surface-to-volume ratio of 6.0 relative to that of the normal vessel, which is equal to 1.0 (Table 2). The effect of a free radical inhibitor is described in Table 3. The kinetic determinations were carried out in the presence of at least 2 equiv. of toluene in order to inhibit any possible free-radical chain process of the substrate and/or products. No

induction period was observed. The rate coefficients are reproducible with a relative standard deviation not greater than $\pm 5\%$ at a given temperature.

The overall rate coefficients determined in seasoned vessels and in the presence of toluene were found to be invariable with the initial pressure of the substrate (Table 4), and the first-order plots are satisfactorily linear up to about 60% reaction. Beyond this percentage decomposition, the relative standard deviation is greater than $\pm 5\%$. The variation of the overall rate coefficient with temperature is given in Table 5, where rate coefficients at the 90% confidence level obtained with a least-squares procedure are given.

The partial rates for the formation of the products as described in reaction (2) were determined, up to 60% decomposition of the substrate, by the quantitative chromatographic analyses of *N*-phenylpyrrolidine and 4-(*N*-methyl-*N*-phenylamino)-1-butene. The variation of

Table 4. Variation of rate coefficients with initial pressure

<i>4-(N-Methyl-N-phenylamino)-1-butyl acetate at 379.2 °C:</i>				
P_0 (Torr)	36	52.5	72.5	95.0
$10^4 k_1$ (s ⁻¹)	11.47	11.86	11.58	11.72
<i>4-(N-phenylamino)-1-butyl acetate at 370.1 °C:</i>				
P_0 (Torr)	23.8	40.5	64.5	82.0
$10^4 k_1$ (s ⁻¹)	5.61	5.42	5.57	5.53

Table 5. Temperature dependence of rate coefficients^a

<i>4-(N-Methyl-N-phenylamino)-1-butyl acetate:</i>					
Temperature (°C)	359.7	370.1	379.2	389.5	399.4
$10^4 k_1$ (s ⁻¹)	3.60	6.92	11.86	21.23	38.66
Rate equation: $\log[k_1 \text{ (s}^{-1}\text{)}] = (13.92 \pm 0.36) - [(210.4 \pm 4.5) \text{ kJ mol}^{-1}](2.303RT)^{-1}$; $r = 0.9999$					
<i>4-(N-Phenylamino)-1-butyl acetate:</i>					
Temperature (°C)	359.9	370.1	380.8	389.5	399.6
$10^4 k_1$ (s ⁻¹)	3.16	5.57	9.55	15.33	27.29
Rate equation: $\log[k_1 \text{ (s}^{-1}\text{)}] = (12.03 \pm 0.43) - [(188.3 \pm 5.3) \text{ kJ mol}^{-1}](2.303RT)^{-1}$; $r = 0.9997$					

^aSeasoned vessel and in the presence of toluene inhibitor.

Table 6. Variation of rate coefficients with temperature for formation of products from 4-(*N*-methyl-*N*-phenylamino)-1-butyl acetate

Temperature (°C)	$10^4 k_1$ (s ⁻¹)	
	<i>N</i> -Phenylpyrrolidine	4-(<i>N</i> -Methyl- <i>N</i> -phenylamino)-1-butene
359.7	2.24	1.36
370.1	4.30	2.62
379.2	7.38	4.48
389.5	13.27	8.06
399.4	24.05	14.61

the rate coefficients for the formation of these products with temperature (Table 6) gives, by the least-squares method and with 90% confidence coefficient, the following Arrhenius expressions:

for *N*-phenylpyrrolidine:

$$\log[k_1 \text{ (s}^{-1}\text{)}] = (13.72 \pm 0.35) - [(210.4 \pm 4.4) \text{ kJ mol}^{-1}](2.303RT)^{-1};$$

$$r = 0.9999$$

for 4-(*N*-methyl-*N*-phenylamino)-1-butene:

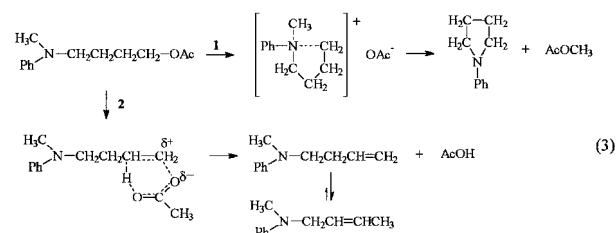
$$\log[k_1 \text{ (s}^{-1}\text{)}] = (13.50 \pm 0.37) - [(210.4 \pm 4.6) \text{ kJ mol}^{-1}](2.303RT)^{-1};$$

$$r = 0.9999$$

Based on the products formed and the kinetic parameters, two different mechanisms are considered (reaction (3)).

Path **1** is analogous to the reaction described for 4-(*N,N*-dimethylamino)-1-butyl acetate,¹ where the bond

polarization $\text{C}^{\delta+} \cdots \text{O}^{\delta-}$ is rate determining. The incipient positive carbon atom is stabilized through anchimeric



assistance by the methylphenylamino group to form an intimate ion-pair intermediate. The acetoxy ion proceeds through intramolecular solvation or autosolvation to attack the CH₃ of C₆H₅(CH₃)N group and form methyl acetate and *N*-phenylpyrrolidine. With regard to Path **2**, the mechanism may be explained as commonly described for ester pyrolysis, involving a semi-polar six-membered cyclic transition state reaction.

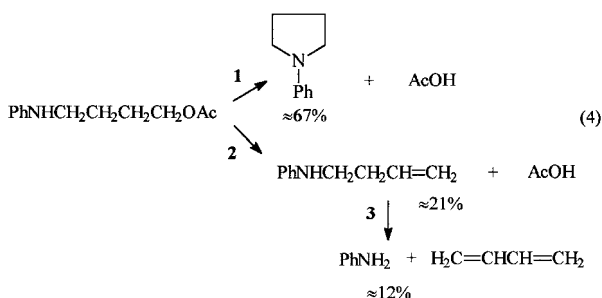
4-(*N*-Phenylamino)-1-butyl acetate

One of the products obtained from the gas-phase

Table 7. Variation of rate coefficients with temperature for formation of products from 4-(*N*-phenylamino)-1-butyl acetate

Temperature(°C)	$10^4 k_1$ (s ⁻¹)		
	<i>N</i> -Phenylpyrrolidine	4-(<i>N</i> -Phenylamino)-1- butene	Aniline
359.9	2.13	0.66	0.38
370.1	3.75	1.16	0.66
380.8	6.42	1.99	1.13
389.5	10.31	3.20	1.82
399.6	17.75	5.51	3.14

pyrolysis of 4-(*N*-phenylamino)-1-butyl acetate described in reaction (4), butadiene (reaction (4), path 3), polymerizes to some extent. However, verification of stoichiometry (4) was possible, when obtaining, up to 60% decomposition, good agreement between pressure measurements and the quantitative titration analysis of acetic acid (Table 1) with 0.05 M NaOH solution.



The homogeneity of reaction (4) was examined by using a vessel with a surface-to-volume ratio six times greater than that of the unpacked vessel. The clean packed and unpacked Pyrex vessels showed a significant effect on the rates (Table 2). However, the packed and unpacked vessels seasoned with allyl bromide no effect on the rate coefficients (Table 2). The addition of different proportions of the free radical suppressor toluene (Table 3) also showed no effect on rates, even though the pyrolysis experiments were carried out in the presence of at least an equal amount of toluene to prevent any possible radical chain reaction. Moreover, no induction period was detected.

The overall rate coefficients for elimination showed no significant variation with change of initial pressure (Table 4), and the first-order plots of $\log(2P_0 - P_t)$ vs time t are linear up to 55% decomposition. Further decomposition leads to a relative standard deviation greater than $\pm 5\%$. The temperature dependence of the overall rate coefficients is described in Table 5, which gives rate coefficients at the 90% confidence level from a least-squares method.

The partial rates of product formation depicted in reaction (4) were determined, up to 55% decomposition, by the quantitative chromatographic analyses of *N*-phenylpyrrolidine, 4-(phenylamino)-1-butene and aniline. The variations of the rate coefficients for the formation of

these products with temperature are given in Table 7 (90% confidence coefficient from the least-squares procedure) and their corresponding Arrhenius equations are as follows: for *N*-phenylpyrrolidine:

$$\log[k_1(\text{s}^{-1})] = (11.84 \pm 0.44) - [(188.1 \pm 5.5) \text{ kJ mol}^{-1}] (2.303RT)^{-1};$$

$$r = 0.9997$$

for 4-(*N*-phenylamino)-1-butene:

$$\log[k_1(\text{s}^{-1})] = (11.36 \pm 0.44) - [(188.3 \pm 5.5) \text{ kJ mol}^{-1}] (2.303RT)^{-1};$$

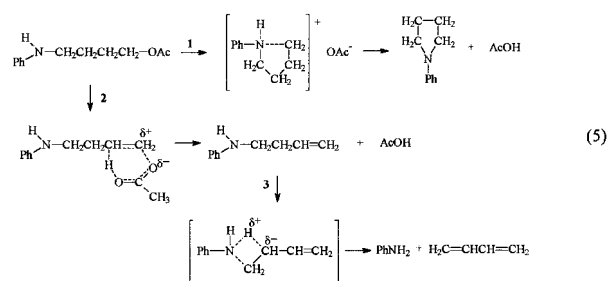
$$r = 0.9997$$

for aniline:

$$\log[k_1(\text{s}^{-1})] = (11.05 \pm 0.51) - [(187.5 \pm 6.3) \text{ kJ mol}^{-1}] (2.303RT)^{-1};$$

$$r = 0.9996$$

The products obtained from this substrate [reaction (4)], together with the kinetic parameter determinations, suggested three different mechanisms [reaction (5)].



The formation of *N*-phenylpyrrolidine may be explained as before, that is, through neighboring group participation of the phenylamino group as described in path 1, reaction (5). An intimate ion-pair type of mechanism appears to be the process for this decomposition. The mechanism for the production of phenylamino-1-butene may be explained in the usual manner as for the pyrolytic elimination of carboxylic esters, which is through a six-

Table 8. Comparative kinetic parameters for neighbouring group participation at 380.0 °C

Substrate	$10^4 k_1$ (s ⁻¹)	E_a (kJmol ⁻¹)	logA (s ⁻¹)	Reference
(CH ₃) ₂ NCH ₂ CH ₂ CH ₂ CH ₂ OAc	678.19	163.5 ± 4.8	11.91 ± 0.43	1
Ph(CH ₃)NCH ₂ CH ₂ CH ₂ CH ₂ OAc	7.76	210.4 ± 4.4	13.72 ± 0.35	This work
PhNHCH ₂ CH ₂ CH ₂ CH ₂ OAc	6.22	188.1 ± 5.5	11.84 ± 0.44	This work

membered cyclic transition state as described in path **2**. The phenylamino-1-butene appears to undergo a partial consecutive decomposition (path **3**) to give aniline and 1,3-butadiene. The mechanism of this process may be rationalized in terms of a discrete four-membered cyclic transition state as shown in reaction (5) path **3**.

The comparative influence of the N atom for neighbouring group participation may be appreciated in Table 8. Apparently, these results suggest that the lower the nucleophilicity of the amino substituent the less is its anchimeric assistance in the stabilization of the polarized C_α—O bond in the transition state. This argument may be justified when the CH₃ group of the (CH₃)₂N substituent is replaced by a phenyl group. The electron delocalization of the nitrogen lone pair in the aromatic ring reduces its availability for anchimeric assistance. Consequently, a decrease in the rate of elimination is obtained. This consideration is consistent with the order of rate coefficients [(CH₃)₂N > C₆H₅(CH₃)N ≥ C₆H₅NH] in Table 8 from their anchimeric at the 4-position for elimination. This sequence appears to be contrary to that expected on the basis of steric acceleration, a factor previously considered and discarded in previous work.⁵

EXPERIMENTAL

4-(Phenylamino)-1-butyl acetate. A solution of 4-bromobutyl acetate (19.5 g., 0.05 mol) and aniline (4.65 g., 0.05 mol) in 20 ml of toluene was refluxed for 9–12 h. The reaction mixture was acidified with 10% hydrochloric acid. The toluene layer was separated and the aqueous layer basified by slow addition of solid sodium hydrogencarbonate. Several extracts with diethyl ether and dried over sodium sulfate were concentrated *in vacuo*. The product was distilled several times to 98.9% purity by GLC. B.p. 120 °C at 0.75 Torr, yield 56–65 %. ¹H NMR(CDCl₃), δ 1.54–1.78 (m, 4H, 2CH₂), 2.02 (s, 3H, COCH₃), 3.17–3.38 (t, 2H, CH₂) 3.96–4.16 (t, 2H, CH₂), 5.53 (bs, 1H, NH), 6.56–6.76 (m, 3H, Ar H), 7.05–7.37 (m, 2H, Ar H). MS, *m/z* 207 (M⁺), 148 (C₆H₅NHCH₂CH₂CH₂CH₂⁺), 106 (C₆H₅NHCH₂⁺), 91 (C₆H₅N⁺), 77 (C₆H₅⁺), 43 (CH₃CO⁺).

4-(N-Methyl-N-Phenylamino)-1-butyl acetate. A solution of 4-bromobutyl acetate (9.75 g., 0.05 mol) and *N*-methylaniline (5.36 g., 0.05 mol) in 15 ml of toluene was refluxed for 10–12 h. The reaction mixture was acidified

with 10% hydrochloric acid. The toluene layer was separated and the aqueous layer treated by slow addition of sodium hydrogencarbonate. The aqueous solution was extracted several times with diethyl ether, dried over sodium sulfate and evaporated *in vacuo*. The product was distilled several times (b.p. 140 °C at 0.75 Torr, yield 72%) and the fraction with 99.9% purity as determined by GLC was used. ¹H NMR(CDCl₃) δ 1.48–1.78 (m, 4H, 2CH₂), 2.02 (s, 3H, CH₃), 2.91 (s, 3H, N-CH₃), 3.09–3.43 (t, 2H, CH₂), 3.97–4.12 (t, 2H, CH₂), 6.58–6.75 (m, 3H, ArH), 7.09–7.36 (m, 2H, ArH). MS, *m/z* 221 (M⁺), 206 [(C₆H₅)CH₃N(CH₂)₄OCO⁺], 162 [(C₆H₅)CH₃N(CH₂)₄⁺], 120 ((C₆H₅)CH₃NCH₂⁺ 106 (C₆H₅NCH₃⁺), 91 (C₆H₅N⁺), 77 (C₆H₅⁺), 43 (CH₃CO⁺).

The quantitative analyses and identifications of substrates and products were carried out by GLC MS (Saturn 2000, Varian). Capillary column: DB-5MS, 30 m × 0.250 mm i.d., 0.25 μm. The internal standard used for quantitative GC analyses was pyrrolidine.

Kinetics. The aminobutyl acetates were pyrolyzed in a static reaction apparatus as previously described,^{6,7} but with some modifications and additions of modern electronic and electrical devices. The reaction vessel was seasoned with allyl bromide, and the decomposition process was carried out in the presence of toluene as a radical chain inhibitor. The amount of substrate employed for each pyrolytic run was around 0.05–0.1 ml. The temperature was controlled by a resistance thermometer controller, Shinko DIC- PS 25RT, and an OMEGA solid-state relay, Model SSR240AC45, maintained within ±0.2 °C and measured with a calibrated platinum–platinum–13% rhodium thermocouple. No temperature gradient was found along the reaction vessel. The overall rate coefficients for 4-(*N*-methyl-*N*-phenylamino)-1-butyl acetate were followed manometrically and the partial rates for the formation of *N*-phenylpyrrolidine and 4-*N*-methyl-*N*-phenylamino-1-butene were obtained by gas chromatographic analyses. The overall rate coefficients for 4-(phenylamino)-1-butyl acetate were determined by pressure increases and the partial rates for the formation of *N*-phenylpyrrolidine, 4-(phenylamino)-1-butene and aniline by gas chromatographic analyses. The substrates were injected with a syringe through a silicone-rubber septum directly into the reaction vessel.

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