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Neighboring group participation in the gas phase. The homogeneous elimination kinetics of 5-(*N*-phenylamino)-1-pentyl acetate and 5-(*N*-methyl-*N*-phenylamino)-1-pentyl acetate

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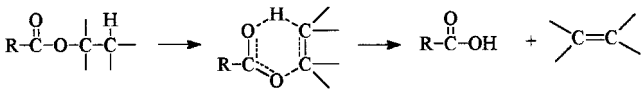
ABSTRACT: The elimination kinetics of the title compounds were determined over the temperature range 370–420 °C and pressure range of 36–91 Torr (1 Torr = 133.3 Pa). The reactions carried out in seasoned vessels with the free radical suppressor toluene always present are homogeneous, unimolecular and obey a first-order rate law. The overall rate coefficient is expressed by the following Arrhenius equations: for 5-(*N*-phenylamino)-1-pentyl acetate, $\log k_1\ (s^{-1}) = (13.56 \pm 0.19) - (211.8 \pm 2.2)\ kJ\ mol^{-1}\ (2.303RT)^{-1}$ and for 5-(*N*-methyl-*N*-phenylamino)-1-pentyl acetate, $\log k_1\ (s^{-1}) = (12.29 \pm 0.41) - (182.9 \pm 5.2)\ kJ\ mol^{-1}\ (2.303RT)^{-1}$. The formation of *N*-phenylpiperidine in both reactions suggests the anchimeric assistance of the PhNH and $Ph(CH_3)N$ groups for a backside displacement. An intimate ion-pair type of mechanism is assumed in the pyrolytic elimination of these phenylaminoalkyl acetates. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: neighboring group participation; gas phase; homogeneous elimination; kinetics; phenylaminopentyl acetates

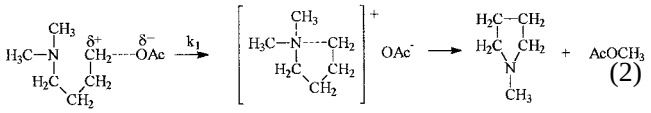
INTRODUCTION

It is well known that the homogeneous unimolecular gas-phase pyrolysis of carboxylic esters generally leads to the formation of the corresponding olefin and carboxylic acid:[1,2]



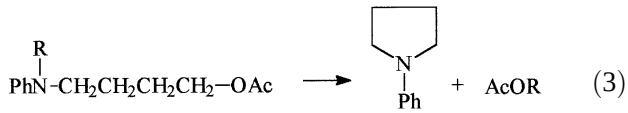
(1)

However, the presence of a $(CH_3)N$ substituent at the 4-position of butyl acetate, i.e. 4-*N*,*N*-dimethylaminobutyl acetate, was found to assist anchimerically a *trans*-elimination process as described in reaction (2).[3] The formation of *N*-methylpyrrolidine and methyl acetate was explained in terms of a modest intimate ion-pair intermediate, where the acetoxy leaving leaving group proceeds by an intramolecular solvation or autosolvation to give the products described in reaction (2).



(2)

Along this line of thought, an additional study[4] was carried out to examine the influence of the phenyl group at the N atom for neighboring group participation in the pyrolytic elimination of 4-(*N*-phenylamino)-1-butyl acetate ($PhNHCH_2CH_2CH_2CH_2OAc$) and 4-(*N*-methyl-*N*-phenylamino)-1-butyl acetate [$Ph(CH_3)NCH_2CH_2CH_2CH_2OAc$]:



$R = H, CH_3$

While this work was in progress, our findings of a substituent effect in the gas-phase pyrolysis of aryl-aminobutyl and arylaminopentyl acetates[5] revealed the

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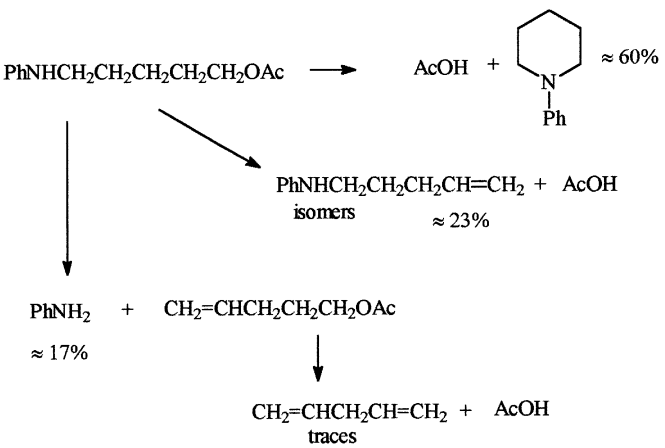
anchimeric assistance of the arylamino substituent for a *trans*-elimination. Moreover, the greater the electron delocalization of the substituent at the 4-position of the benzene ring, the more effective is the participation and the faster the elimination rate. The mechanism was explained in terms on an intimate ion-pair intermediate.

Since a six-membered structure is less favored than a five-membered structure in neighboring group participation,[6] the present work was addressed at examining the extent to which these PhNH and $Ph(CH_3)N$ groups at the 5-position of alkyl acetates, i.e., $PhNHCH_2CH_2CH_2CH_2CH_2OAc$ and $Ph(CH_3)NCH_2CH_2CH_2CH_2CH_2OAc$, may assist anchimerically the elimination process of these substrates in the gas phase.

RESULTS AND DISCUSSION

5-(*N*-Phenylamino)-1-pentyl acetate

The molecular decomposition of this substrate in the gas phase proceeds according to reaction (4):



(4)

The stochiometry of Eqn. (4) requires that for long reaction time $P_f/P_o = 2.0$, where P_f and P_o are the final and initial pressures, respectively. The average experimental results at four different temperatures and 10 half-lives is 2.0 (Table 1). Additional examination of the above stoichiometry of Eqn. (4) was made by comparing, up to 30% decomposition, the pressure measurements with the results of quantitative titration of acetic acid with 0.05 M NaOH solution (Table 2).

The effect of the surface on the rate of decomposition was tested by carrying out several runs in a vessel with a surface-to-volume ratio of 6.0 relative to that of the normal vessel, which is equal to 1.0. Packed and unpacked Pyrex vessels seasoned with allyl bromide showed no effect on the reaction rates. However, packed and unpacked clean Pyrex vessels had a marked heterogeneous effect on the rate coefficient of 5-(*N*-phenylamino)-1-pentyl acetate (Table 3).

The effect of the free radical inhibitor toluene is shown in Table 4. The kinetic runs had to be carried out with at least a threefold excess of toluene in order to prevent any free radical processes of the substrate and/or products. No induction period was observed. The rate coefficients were reproducible with a relative standard deviation of $\pm 5\%$ at any given temperature.

The first-order rate coefficient of this substrate calculated from $k_1 = -(2.303/t) \log [(2P_o - P_t)/P_o]$ was independent of the initial pressure (Table 5). A plot of $\log(2P_o - P_t)$ against time t gave a good straight line up to 60% reaction. The variation of the overall rate coefficient with temperature is shown in Table 6, where the rate coefficients at the 90% confidence limit obtained by a least-squares procedure are given.

The partial rates for the formation of the products as described in reaction (4) were determined up to 60% decomposition of the substrate by the quantitative chromatographic analysis of *N*-phenylpiperidine, 5-(phenylamino)pentenes and aniline. The variation of the rate coefficients for the formation of these products with temperature (Table 7) gives by the least-squares procedure and with 90% confidence the following

Table 1. Ratio of rate of final (P_f) to initial (P_o) pressure.[a]

Substrate	Temperature (°C)	P_o (Torr)	P_f (Torr)	P_f/P_o	Average
5-(*N*-Phenylamino)-1-pentyl acetate	391.2	78	155.5	1.99	2.01
	407.7	48	92	1.92	
	410.2	61	119	1.95	
	420.0	62	136	2.19	
5-(*N*-Methyl-*N*-phenylamino)-1-pentyl acetate	389.6	47.5	108	2.27	2.27
	399.7	41	88.5	2.16	
	410.0	44	99	2.25	
	420.0	58.5	139.5	2.38	

[a] Vessel seasoned with allyl bromide and in the presence of toluene inhibitor. 1 Torr = 133.3 Pa.

Table 2. Stoichiometry of the reactions

5-(N-Phenylamino)-1-pentyl acetate at 400.7°C:					
Time (min)	1.5	3	5		
Reaction (%) (pressure)	11.5	21.9	31.3		
Acetic acid (%) (titration)	9.8	18.9	30.2		
5-(N-Methyl-N-phenylamino)-1-pentyl acetate at 399.7°C:					
Time (min)	3	5	10	12	15
Reaction (%) (pressure)	15.8	24.2	43.5	49.5	57.3
Acetic acid (%) (GC)	12.5	16.5	29.5	33.7	37.9
Methyl acetate (%) (GC)	5.0	7.8	13.9	16.4	18.9

Table 3. Homogeneity of the reactions

Compound	S/V (cm^{-1})[a]	$10^4 k_1(s^{-1})$[b]	$10^4 k_1(s^{-1})$[c]
5-(N-Phenylamino)-1-pentyl acetate at 391.2°C	1	19.67[d]	7.90
	6	12.56[d]	8.06
5-(N-Methyl-N-Phenylamino)-1-pentyl acetate at 399.7°C	1	14.91	15.40
	6	15.77	15.67

[a] S = surface area; V = Volume.
[b] Clean Pyrex vessel.
[c] Vessel seasoned with allyl bromide.
[d] Average k value.

Table 4. Effect of the inhibitor toluene on rates[a]

Substrate	P_o (torr)	P_i (torr)	P_i/P_o	$10^4\ k_1\ (s^{-1})$
5-(N-phenylamino)-1-pentyl acetate at 400.7°C	45	—	—	13.52[b]
	52.5	154.5	2.9	13.43[c]
	48	178	3.7	13.59[c]
	30	128.5	4.3	13.54[c]
	36	185	5.1	13.36[c]
5-(N-Methyl-N-phenylamino)-1-pentyl acetate at 389.6°C	92	—	—	5.32
	80	79	1.0	5.82
	71	139	2.0	8.00
	43	114.5	2.7	9.64
	47.5	175.0	3.7	9.52

[a] P_0 = pressure of the substrate; P_i = pressure of toluene inhibitor. Vessel seasoned with allyl bromide.
[b] k-Value up to 20% reaction.
[c] k-value up to 60% reaction.

Table 5. Variation of overall rate coefficients with initial pressure

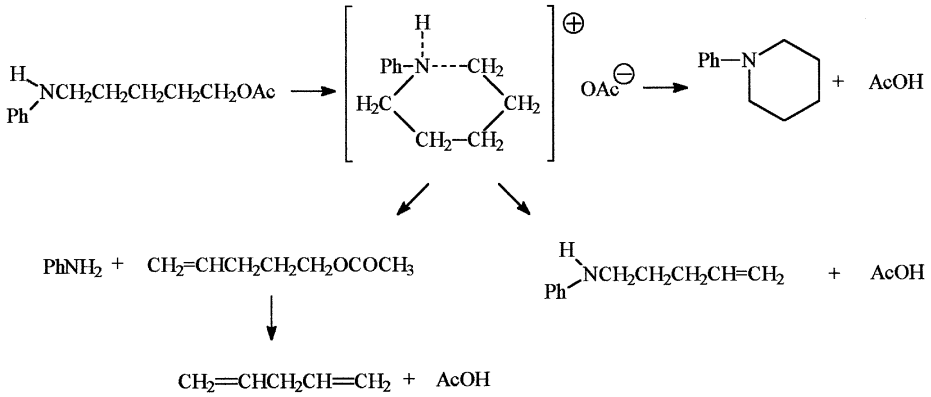
5-(N-Phenylamino)-1-pentyl acetate at 400.7°C:					
P_o (torr)	36	48	52.5	70	91
$10^4\ k_1\ (s^{-1})$	13.36	13.59	13.93	13.71	13.70
5-(N-Methyl-N-phenylamino)-1-pentyl acetate at 389.6°C:					
P_o (Torr)	37	47.5	51.5	62	81
$10^4\ k_1\ (s^{-1})$	9.35	9.52	9.70	9.65	9.88

Table 6. Temperature dependence of the overall rate coefficients[a]

5-(N-Phenylamino)-1-pentyl acetate:					
Temperature (°C)	380.0	391.2	400.7	410.2	420.0
$10^4\ k_1\ (s^{-1})$	4.10	7.90	13.59	22.68	39.20
Rate equation: $\log k_1\ (s^{-1}) = (13.56 \pm 0.17) - (211.8 \pm 2.2)\ kJ\ mol^{-1}\ (2.303RT)^{-1}$; $r = 0.99997$					

5-(N-Methyl-N-phenylamino)-1-pentyl acetate:						
Temperature (°C)	370.1	380.1	389.6	399.7	410.0	420.4
$10^4\ k_1\ (s^{-1})$	3.18	5.59	9.62	15.40	25.90	45.84
Rate equation: $\log k_1\ (s^{-1}) = (12.29 \pm 0.48) - (182.9 \pm 5.2)\ kJ\ mol^{-1}\ (2.303RT)^{-1}$; r = 0.99964						

[a] Seasoned vessel and in the presence of toluene inhibitor.



(5)

Arrhenius equations:

for N-phenylpiperidine:

$$\log k_1(s^{-1}) = (13.23 \pm 0.10) - (210.3 \pm 1.3)\,\text{kJmol}^{-1}(2.303RT)^{-1}; r = 0.99997$$

for 5-(N-phenylamino)-1- and 2-pentene:

$$\log k_1(s^{-1}) = (12.82 \pm 0.14) - (210.6 \pm 1.9)\,\text{kJmol}^{-1}(2.303RT)^{-1}; r = 0.99997$$

for aniline:

$$\log k_1(s^{-1}) = (12.63 \pm 0.18) - (210.3 \pm 2.3)\,\text{kJmol}^{-1}(2.303RT)^{-1}; r = 0.99996$$

Product analysis and kinetic data for reaction (4) suggest two different mechanisms (see eqn. 5 above).

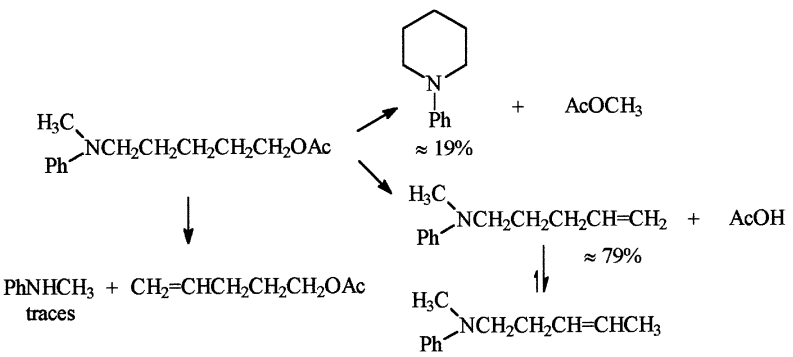
Since the bond polarization of C $^{\delta+}$ … O $^{\delta-}$ may be rate determining, the discrete carbocation is stabilized through the anchimeric assistance of the phenylamino susbtituent. Apparently, an intimate ion-pair mechanism seems to be the process of decomposition, leading to the formation of products described in reaction (5).

5-(*N*-Methyl-*N*-phenylamino)-1-pentyl acetate

The experimental stoichiometry for the elimination of 5-(*N*-methyl-*N*-phenylamino)-1-pentyl acetate in the gas phase [reaction (6)] demands $P_f/P_o = 2.0$ (see eqn 6 below).

The average P_f/P_o at four different temperatures and 10 half-lives was 2.27 (Table 1). The small departure from the theoretical stochiometry was due to the formation of very small amounts of methylaniline, dimethylaniline and methylphenylacetamide. However, a check of stoichiometry of reaction (6), up to 60% decomposition, was possible by comparing the pressure measurements with the sum of the quantitative chromatographic analyses of acetic acid and methyl acetate (Table 2).

Table 3 indicates that reaction (6) is homogeneous, since no significant variation of the rates was observed in the experiments when using both clean Pyrex and seasoned Pyrex vessels with a surface-to-volume ratio of 6.0 relative to that of the normal vessel. The effect of the free radical suppressor is shown in Table 4. The kinetic determination had to be carried out in the



(6)

Table 7. Variation of rate coefficients with temperature for formation of products from 5-(*N*-phenylamino)-1-pentyl acetate

	$10^4\ k_1\ (s^{-1})$		
Temperature (°C)	*N*-Phenylpiperidine	5-(*N*-Phenylamino)-1- and 2-pentene	Aniline
380.0	2.59	0.95	0.66
391.2	4.92	1.81	1.25
400.7	8.37	3.08	2.13
410.2	14.23	5.24	3.62
420.0	24.19	8.90	6.16

presence of toluene (the concentration of toluene is at least three times the initial pressure of the 5-(*N*-methyl-*N*-phenylamino)-pentyl acetate, to inhibit any possible chain processes of the substrate and/or the products (Table 4). No induction period was observed. The rate coefficients are reproducible with a relative standard deviation not greater than ±5% at a given temperature.

The rate coefficient also calculated from $k_1 = -(2.303/t)\log[(2P_o - P_t)/P_o]$ was independent of their initial pressure. When plotting $\log(2P_o - P_t)$ against time t, a good straight line, up to 55% reaction, was obtained (Table 5). The temperature dependence of the rate coefficient and the corresponding Arrhenius equation is given in Table 6 (90% confidence coefficient from the least-squares procedure).

To determine the partial rates of product formation from the pyrolysis of this substrate, up to 55% decomposition, the rate of elimination towards *N*-phenylpiperidine and *N*-methyl-*N*-phenylaminopentenes [reaction (6)] was estimated by the quantitative chromatographic analyses of these products. The temperature dependence of the rate coefficients for product formation are given in Table 8. The Arrhenius equation (90% confidence coefficient from the least-squares procedure) are given as follows:

for N-phenylpiperidine:

$$\log k_1(s^{-1}) = (11.59 \pm 0.42) - (194.5 \pm 5.4)\,\text{kJmol}^{-1}(2.303RT)^{-1};\ r = 0.99996$$

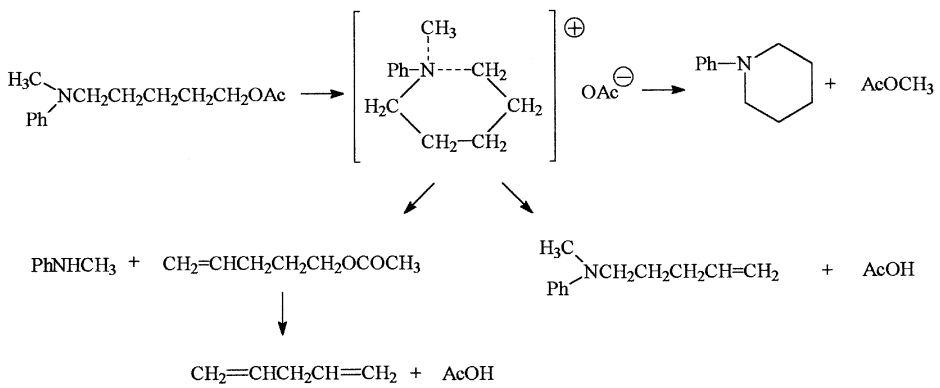
for 5-(N-methyl-N-phenylamino)pentenes:

$$\log k_1(s^{-1}) = (12.19 \pm 0.41) - (194.3 \pm 5.2)\,\text{kJmol}^{-1}(2.303RT)^{-1};\ r = 0.99997$$

see equation 7 below.

According to product formation analysis of this substrate [reaction (6)], together with the kinetic data, one can suggest a mechanism with a common intermediate as described in reaction (7). The neighboring group participation of the *N*-methyl-*N*-phenylmino group may lead to the formation of *N*-phenylpiperidine, 5-(*N*-methyl-*N*-phenylamino)-1- and -2-pentenes, and traces of *N*-methylaniline.

As reported before,[4] the order in rate elimination through the anchimeric assistance of the N atom in the gas-phase pyrolysis of 4-substituted phenylaminobutyl acetates was $(CH_3)_2N > PhCH_3N \geq PhNH$ (Table 9). This sequence is contrary to the neighboring group participation of the 5-substituted aminopentyl acetates obtained in the present work, i.e. $PhNH > PhCH_3N$. Since the six-membered structure is less favored than the 5-membered structure in neighboring group participation,[6] the nucleophilicity of the amino substituent at the 5-position may not be so effective in its anchimeric assistance and in the stabilization of the polarized $C^{\delta+} \ldots O^{\delta-}$ bond intermediate. This appears to suggest that steric factors cause more difficulty for the formation of the cyclic product *N*-phenylpiperidine.



(7)

Table 8. Variation of rate coefficients with temperature for formation of products from *5-(N-methyl-N-phenylamino)-1-pentyl acetate*

	$10^4 k_1$ (s^{-1})	
Temperature (°C)	*N*-Phenylpiperidine	5-(*N*-Methyl-*N*-phenylamino)-1- and 2-pentene
370.1	0.62	2.56
380.1	1.10	4.49
389.6	1.89	7.73
399.7	3.02	12.38
410.0	5.08	20.82
420.4	8.98	36.86

EXPERIMENTAL

5-(N-Phenylamino)-1-pentyl acetate. A solution of 5-bromopentyl acetate (10.45 g., 0.05 mol) and aniline (4.65 g, 0.05 mol) in 20 ml. of toluene was refluxed for 10 h. The solution was cooled and acidified with 10% hydrochloric acid. The toluene layer was separated and the aqueous layer was basified by the slow addition of solid sodium hydrogencarbonate. It was then repeatedly extracted with diethyl ether, dried over sodium sulfate and concentrated *in vacuo*. The product was purified by distillation to give 5-(*N*-phenylamino)-1-pentyl acetate at 140C °C/0.73 mbar in 60% yield. Anal. Calcd for $C_{13}H_{19}NO_2$ (221), C, 70.59; H, 8.59; N, 6.63. Found: C,70.49; H, 8.43; N, 6.56%. ^{1}H NMR ($CDCl_3$): δ 1.36–1.78 (m, 6H, $3CH_2$), 2.03 (s, 3H, CH_3), 3.01–3.20 (t, 2H, CH_2), 3.98–4.19 (t, 2H, CH_2) 6.52–6.72 (m, 3H, Ar-H), 7.03–7.21 (m, 2H, Ar-H). MS, *m/z* 221 (M^+), 162 [($PhNH(CH_2)_5^+$], 120 ($PhNHCH_2CH_2^+$), 106 ($PhNHCH_2^+$), 77 (Ph^+), 43 (CH_3CO^+).

5-(N-Methyl-N-phenylamino)-5-pentyl acetate. A solution of 5-bromopentyl acetate (10.45 g, 0.05 mol) and N-methylaniline (5.36 g, 0.05 mol) in 15 ml of toluene was refluxed for 10 h. The solution was acidified with 10% hydrochloric acid. The toluene layer was separated and the aqueous solution was basified by the slow addition of solid sodium hydrogencarbonate. It was then repeatedly extracted with diethyl ether, dried over sodium sulfate and concentrated *in vacuo*. The product was purified by distillation to afford 5-(*N*-methyl-*N*-phenylamino)-1-pentyl acetate at 122–124 °C/0.6 mbar in 75% yield. Anal. Calcd for $C_{14}H_{21}NO_2$ (235), C, 71.48; H, 8.93; N. 5.95. Found: C, 71.21; H, 8.72; N, 6.26%. ^{1}H NMR ($CDCl_3$): δ 1.41–1.81 (m, 6H, $3CH_2$), 2.05 (s, 3H, CH_3), 2.92 (s, 3H, N-CH_3), 306-3.41 (t, 2H, CH_2), 3.92–4.09 (t, 2H, CH_2) 6.56–6.81 (m, 3H, Ar-H), 7.10–7.36 (m, 2H, Ar-H). MS, *m/z* 235 (M^+), 220 [$PhN(CH_2)_5OAc^+$], 162 [$PhN(CH_3)(CH_2)_4^+$], 120 [$PhN(CH_3)CH_2^+$], 106 [$PhN(CH_3)^+$], 77 (Ph^+), 43 (CH_3CO^+).

The quantitative analyses and identifications of substrates and products were determined by gas chromatography–mass spectrometry with a Saturn 2000, instrument (Varian) using a DB-5MS capillary column 30 m × 0.250 mm i.d., 0.25 μm film thickness. The internal standard used for quantitative GC analysis was piperidine.

Kinetics. The kinetic experiments were carried out in a static reaction system as described previously,[7,8] with some modifications and additions of modern electronic and electrical devices. The reaction vessel was seasoned with the product of decomposition of allyl bromide and each pyrolytic run was carried out in the presence of the free radical chain suppressor toluene. The amount of the aminopentyl acetate employed for each decomposition process was around 0.05–0.1 ml. The temperature was controlled by a Shinko DIC-PS 25RT resistance thermometer controller and an Omega Model SSR240AC45 solid-state relay, maintained within ±0.2 °C and

Table 9. Comparative kinetic parameters for neighboring group participation at 380.0 °C

Substrate	$10^4 k_1$ (s^{-1})	E_a, kJ mol^{-1}	Log *A*, (s^{-1})	Ref.
$(CH_3)_2NCH_2CH_2CH_2CH_2OAc$	678.19	163.5 ± 4.8	11.91 ± 0.43	3
$PhNHCH_2CH_2CH_2CH_2OAc$	6.22	188.1 ± 5.5	11.84 ± 0.44	4
$PhNHCH_2CH_2CH_2CH_2CH_2OAc$	2.57	210.3 ± 1.3	13.23 ± 0.10	This work
$Ph(CH_3)NCH_2CH_2CH_2CH_2OAc$	7.76	210.4 ± 4.4	13.72 ± 0.35	4
$Ph(CH_3)NCH_2CH_2CH_2CH_2CH_2OAc$	1.07	194.5 ± 5.4	11.59 ± 0.42	This work

measured with a calibrated platinum–platinum–13% rhodium thermocouple. No temperature gradient was found along the reaction vessel. The overall rate coefficients for 5-(*N*-phenylamino)-1-pentyl acetate were determined by pressure increase and the partial rates for the products *N*-phenylpiperidine and 5-(*N*-phenylamino)pentenes and aniline were calculated by gas chromatographic analyses. The overall rate coefficients of 5-(*N*-methyl-*N*-phenyamino)-1-pentyl acetate were estimated by pressure increase and the partial rates of formation of *N*-phenylpiperidine and the mixture of *N*-methyl-*N*-phenylaminopentenes by gas chromatographic analyses. The substrates were injected with a syringe directly into the reaction vessel, through a silicone-rubber septum.

Acknowledgements

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