# KINETICS AND MECHANISM OF THE AMINOLYSIS OF *p*-NITROPHENYL *N*-PHENYLCARBAMATES

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Kinetic studies of the reactions of *p*-nitrophenyl *N*-phenylcarbamates with benzylamines were carried out in acetonitrile at 25.0 °C. Second-order  $(k_2)$  and third-order  $(k_3)$  rate constants were observed for all the Y-substituted carbamates except for Y = m - Cl. The relatively large magnitude of  $\rho_X$  (for X-substituted benzylamines) and  $\rho_Y$  together with a positive cross-interaction constant  $\rho_{XY}$  supports a stepwise mechanism involving rate-limiting breakdown of the zwitterionic tetrahedral intermediate T<sup>±</sup>. Kinetic isotope effect studies with deuterated benzylamine (XC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>ND<sub>2</sub>) indicate that in the base-catalyzed path,  $k_3$ , rate-limiting deprotonation occurs at the amino group of benzylamine within the T<sup>±</sup> intermediate. The low  $\Delta H^*$  and  $\Delta S^*$  values for the  $k_3$  process are in accord with the proposed mechanism. © 1997 John Wiley & Sons, Ltd.

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#### INTRODUCTION

Although the mechanism of the aminolysis of aryl esters<sup>1</sup> (1) and carbonates<sup>2</sup> (2) have been investigated extensively, reports on the aminolysis mechanism of N-phenylcarbamates (3) are scarce. These three classes of carbonyl compounds differ only in the acyl part , R, RO and RNH, where R is alkyl or aryl, with a similar phenoxy leaving group, OAr. The aminolysis mechanism of the carbamates is therefore expected to be similar to the relatively well known aminolysis mechanisms of the esters 1 and carbonates 2. Shawali et al.3 proposed a stepwise mechanism with ratelimiting breakdown of a tetrahedral intermediate,  $T^{\pm}$ , for the reactions of aryl N-arylcarbamates, R=Ar in 3, with nbutylamine in dioxane. Their kinetic results were compatible with the stepwise mechanism involving two reaction pathways, an overall second-order,  $k_2$ , and an overall third-order,  $k_3$ , process (Scheme 1), which is similar to the aminolysis mechanisms proposed for some of 1 and 2, but is in contrast to an ElcB mechanism proposed by Menger and Glass<sup>4</sup> for the reaction of *p*-nitrophenyl Nphenylcarbamate with diethylamine in toluene. In this latter



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mechanism, an isocyanate is formed instead of a zwitterionic tetrahedral intermediate  $T^{\pm}$  (Scheme 2). We extend here our series of kinetic studies on the effects of acyl group on the mechanism of the aminolysis of carbonyl compounds to the reactions of *p*-nitrophenyl *N*-phenylcarbamates with benzylamines in acetonitrile [equation (1)].

$$\begin{array}{c} \text{YC}_{6}\text{H}_{4}\text{NHCOOC}_{6}\text{H}_{4}\text{Z} + \text{XC}_{6}\text{H}_{4}\text{C}\text{H}_{2}\text{N}\text{H}_{2} & \xrightarrow{\text{MeCN}} \\ & & \\$$

In this work, we apply the mechanistic criteria based on the cross-interaction constants,  $\rho_{ij}$  in equations (2), where *i* and *j* denote the substituents in the nucleophile (X), substrate (Y) and leaving group (Z).<sup>5</sup> The simple secondorder expression

$$\log(k_{ij}/k_{\rm HH}) = \rho_i \sigma_i + \rho_j \sigma_j + \rho_{ij} \sigma_i \sigma_j$$
(2a)

is obtained by a Taylor series expansion of log  $k_{ij}$  around  $\sigma_i = \sigma_j = 0$  and neglecting pure second-order ( $\rho_{ii}$  and  $\rho_{jj}$ ) and higher-order ( $\rho_{iij}$ , etc.) terms. The cross-interaction constant,  $\rho_{ii}$ , can be alternatively defined as<sup>5</sup>

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Scheme 1

(2b)

$$\rho_{ij} = \frac{\partial \rho_j}{\partial \sigma_i} = \frac{\partial \rho_i}{\partial \sigma_i}$$

### **RESULTS AND DISCUSSION**

The reactions of *p*-nitrophenyl *N*-phenylcarbamates (PCB) with benzylamines (BA) in acetonitrile at  $25.0 \text{ }^{\circ}\text{C}$  obey a third-order rate law:

$$rate = k_{obs}[PCB]$$
(3)

$$k_{\rm obs} = k_2 [BA] + k_3 [BA]^2 \tag{4}$$

except for Y = m-Cl, for which  $k_3=0$ . The second and third order-rate constants,  $k_2$  and  $k_3$ , are obtained from a straight line plot of  $k_{obs}/[BA]$  vs [BA] (Figure 1) as the intercept and slope, respectively. For the case of Y=m-Cl, the slope of a plot of  $k_{obs}$  vs [BA] yielded  $k_2$ . The values of  $k_2$  and  $k_3$  are summarized in Tables 1 and 2. The  $k_3$  values are in general greater than the corresponding  $k_2$  values as noted for the similar reaction of esters<sup>1a</sup> (1), halides, <sup>1h</sup> carbonates<sup>6</sup> (2) and carbamates<sup>3</sup> (3).

An isocynate intermediate proposed by Menger and Glass<sup>4</sup> was not found in the analysis of the infrared spectrum ( $2275-2240 \text{ cm}^{-1}$ ). The product studies and the third-order kinetics [equation (4)] observed lead us to a likely mechanism for the present reactions as shown in



 $Ar = p - NO_2 C_6 H_4, R = C_2 H_5$ 

Scheme 2

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Scheme 1, where  $Z=p-NO_2$  and  $R=XC_6H_4CH_2$ . The  $k_3$  step is deprotonation by benzylamine of the tetrahedral intermediate,  $T^{\pm}$ , to yield the anionic intermediate  $T^{-}$ . The  $k_3$ step is the rate-determining step for the right-hand side path of Scheme 1 since breakdown of  $T^{\pm}$  to products should be fast.<sup>6</sup> The proton transfer is fast in water but not in MeCN. As a result, the  $k_3$  step may become competitive with  $k_2$ .<sup>1k,1</sup>

The Hammett ( $\rho_x$  and  $\rho_y$ ) and Brønsted ( $\beta_x$ ) coefficients determined are given in Table 1 for the  $k_2$  step. The exceptionally large magnitudes of these selectivity parameters are consistent with the stepwise mechanism with rate-limiting breakdown of T<sup>±</sup>;<sup>1, 2</sup> both  $\rho_x$  and  $\rho_y$  should be



Figure 1. The plot of  $k_{\rm obs}/[C_6H_5CH_2NH_2]$  vs [benzylamine] for the reaction of *p*-nitrophenyl *N*-phenylcarbamate with benzylamine in acetonitrile at 25·0 °C

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Table 1. Second-order rate constants,  $k_2$  (dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>), for the reactions of *p*-nitrophenyl *N*-(Y)phenylcarbamates with X-benzylamines in acetonitrile at 25.0 °C

		Y			
Х	<i>p</i> -CH <sub>3</sub>	Н	p-Cl	<i>m</i> -Cl	
p-CH <sub>3</sub>	0.403ª			3.57ª	
1 2	0.953	1.23	3.26	8.49	
	2.28b			20·2 <sup>b</sup>	
Н	0.528	0.655	1.89	5.81	
p-Cl	0.201	0.268	0.894	3.20	
m-Cl	$0.0471^{a}$			0.962ª	
	0.112	0.161	0.458	2.29	
	0·267 <sup>b</sup>			5.45 <sup>b</sup>	
$\rho_{\rm x}^{\ \rm c}$	-1.73	-1.63	-1.55	-1.06	
$\beta_{\rm X}{}^{\rm d}$	1.75	1.65	1.56	1.07	

<sup>a</sup> At 15.0 °C.

<sup>b</sup> At 35.0 °C.

<sup>c</sup> The  $\sigma$  values were taken from Ref. 7. Correlation coefficients were better than 0.997 in all cases.

<sup>d</sup> The  $pK_a$  (H<sub>2</sub>O, 25.0 °C) values were taken from Ref. 8. Correlation coefficients were better than 0.997 in all cases.

compared with other corresponding values after taking into account of a non-conjugating intervening group, CH<sub>2</sub> and NH, present in the benzylamine nucleophile and in the *N*-phenylcarbamate substrate respectively, which are known to reduce the  $\rho$  values by a factor of *ca* 2·8.<sup>9</sup> The large  $\beta_X$  values are also in line with the proposed mechanism,<sup>1,2</sup> but they are less reliable since the  $pK_a$  values used are those in water, not in acetonitrile. However, it is well known that although the absolute  $pK_a$  values are different in H<sub>2</sub>O and MeCN, the  $\Delta pK_a = (pK_a)_{MeCN} - (pK_a)_{H_2O}$  values for the structurally similar amines are nearly the same.<sup>10</sup> Thus the  $\beta_X$  values should be nearly the same in both H<sub>2</sub>O and MeCN.<sup>10c</sup>

The 16  $k_2$  values in Table 1 are subjected to multiple regression using equation (2a) with *i*, *j*=X, Y. The result

Table 2. Third-order rate constants,  $k_3$  (dm<sup>6</sup> mol<sup>-2</sup> s<sup>-1</sup>), for the reactions of *p*-nitrophenyl *N*-(Y)phenylcarbamates with X-benzyl-amines in acetonitrile at 25.0 °C

	Y			
Х	<i>p</i> -CH <sub>3</sub>	Н	p-Cl	
p-CH <sub>3</sub>	8.59ª			
. 5	9.45			
	10·4 <sup>b</sup>	10.2	32.3	
Н	5.61	6.37	27.5	
p-Cl	1.51	2.50	7.04	
m-Cl	$1 \cdot 14^{a}$			
	1.28			
	1.43 <sup>b</sup>	1.38	4.98	

<sup>a</sup> At 15.0 °C. <sup>b</sup> At 35.0 °C.

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(correlation coefficient = 0.974):

$$\log(k_{\rm XY}/k_{\rm HH}) = -1.62\sigma_{\rm X} + 1.94\sigma_{\rm Y} + 1.10\sigma_{\rm X}\sigma_{\rm Y} \qquad (5)$$

indicates that  $\rho_{XY}$  is positive and relatively large, which is again in line with the proposed stepwise mechanism; it has been shown both experimentally and theoretically that the sign of  $\rho_{XY}$  should be positive in contrast to the negative  $\rho_{XY}$  for the  $S_N^2$  processes.<sup>5,11</sup> In the bond-making step, a stronger electron acceptor substituent in the substrate  $(\delta\sigma_Y>0)$  invariably leads to a tighter bond with the nucleophile in the TS ( $\delta\rho_X<0$ ) so that  $\rho_{XY} (=\delta\rho_X/\delta\sigma_Y)$  is negative.<sup>5,11</sup> The values of  $\rho_X (-1.62)$  and  $\rho_Y(1.94)$  are in good agreement with the corresponding values in Table 1 determined independently using the simple (first-order) Hammett equation ( $\rho_X = -1.63$ ;  $\rho_Y = 1.92$ ).

For the base-catalyzed process,  $k_3$ , a similar multiple regression analysis yielded a much worse correlation, probably due to complex effects of the substituents. For example, the effects of substituent in nucleophile, X, on the rate of deprotonation is complex since the effect of the catalyst benzylamine should be opposite to that of benzylamine within T<sup>±</sup>.

Kinetic deuterium isotope effects involving amine protons on the second-  $(k_2)$  and third-order  $(k_3)$  rate constants are studied incorporating deuterium isotopes (i) in the substrate amino group,  $YC_6H_4NH(D)COOC_6H_4NO_2$ , and (ii) in the nucleophile amino group,  $XC_6H_4CH_2NH_2(D_2)$ . The results are summarized in Tables 3 and 4. Reference to Table 3 reveals that the isotope effects involving substrate amine protons are small  $(k_{\rm H}/k_{\rm D} \approx 1.10)$  for  $k_2$  and negligible (ca 1.00) for  $k_3$ . The small kinetic isotope effects for  $k_2$ probably arise from the same origin as those found for the deuterated nucleophiles in the stepwise mechanisms of the esters and carbonates; the  $k_{\rm H}/k_{\rm D}$  values are normally slightly greater than unity for such processes, in contrast to inverse effects  $(k_{\rm H}/k_{\rm D} < 1.0)$  observed for the rate-limiting attack process, i.e. for  $S_N 2$  or rate-limiting formation of  $T^{\pm}$ .<sup>5c</sup> The negligible effects for  $k_3$  suggest that the substrate amine proton is not involved in the deprotonation step,  $k_3$ . This is in contrast to the kinetic deuterium isotope effects observed with the deuterated nucleophiles in Table 4. Again for  $k_2$ , the  $k_{\rm H}/k_{\rm D}$  values are similar to those for the deuterated substrate amine in Table 3. However, for the  $k_3$  step, we observe strong primary isotope effects  $(k_{\rm H}/k_{\rm D} \approx 1.7 - 1.8)$ , which can be taken as clear evidence that in the basecatalyzed process,  $k_3$ , deprotonation takes place at the amino group of the nucleophile in the TS. This supports our proposed mechanism presented in Scheme 1 for the reactions of p-nitrophenyl N-phenylcarbamates with benzylamines in acetonitrile.

A relatively strong acceptor in the substrate (Y=*m*-Cl) seems to stabilize the TS ( $k_2$ ) for the uncatalyzed pathway so that the  $k_2$  path becomes predominant over the basecatalyzed process,  $k_3$ . This is reasonable since in the TS ( $k_2$ ) negative charge develops ( $\rho_{\rm Y} > 0$ ) at the carbonyl carbon, which can be delocalized by a stronger acceptor Y.

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Table 3. Kinetic isotope effects on the second-  $(k_2)$  and the third-order rate constants (k3) for the reactions of deuterated p-nitrophenyl N-(Y)phenylcarbamates [YC<sub>6</sub>H<sub>4</sub>NH(D)C(O)OC<sub>6</sub>H<sub>4</sub>-*p*-NO<sub>2</sub>] with X-benzylamines acetonitrile at 25<sup>-</sup>0 °C in

Х	Y	$k_{2(\mathrm{H})} (\mathrm{dm^3  mol^{-1}  s^{-1}})$	$k_{2(D)} (\mathrm{dm^3  mol^{-1}  s^{-1}})$	$k_{ m H}/k_{ m D}$
H H <i>m</i> -Cl <i>n</i> -Cl	H m-Cl H m-Cl	$\begin{array}{c} 0.655 \pm 0.002^{a} \\ 5.80 \pm 0.03 \\ 0.161 \pm 0.004 \\ 2.29 \pm 0.02 \end{array}$	$\begin{array}{c} 0.585 \pm 0.003 \\ 5.60 \pm 0.02 \\ 0.460 \pm 0.004 \\ 2.14 \pm 0.04 \end{array}$	$\begin{array}{c} 1 \cdot 12 \pm 0 \cdot 03^{b} \\ 1 \cdot 04 \pm 0 \cdot 02 \\ 1 \cdot 10 \pm 0 \cdot 05 \\ 1 \cdot 07 \pm 0 \cdot 03 \end{array}$
X	Y	$k_{3(\mathrm{H})} (\mathrm{dm^6  mol^{-2}  s^{-1}})$	$k_{3(D)} (\mathrm{dm^6  mol^{-2}  s^{-1}})$	$k_{ m H}/k_{ m D}$
H m-Cl	H H	$\begin{array}{c} 6{\cdot}37{\pm}0{\cdot}03^{a} \\ 1{\cdot}38{\pm}0{\cdot}02 \end{array}$	$6.34 \pm 0.06$ $1.16 \pm 0.02$	$1.01 \pm 0.04^{b}$ $1.19 \pm 0.03$

Standard deviation b Standard error.



the aminolysis of the esters, halides and carbonates.1e,h, 3, 13 We conclude that the aminolysis of p-nitrophenyl Nphenylcarbamates in acetonitrile proceeds by a stepwise mechanism with rate-limiting breakdown of the zwitterionic tetrahedral intermediate,  $T^{\pm}.$  The breakdown step can be either base-catalyzed  $(k_3)$  or uncatalyzed  $(k_2)$ .

## **EXPERIMENTAL**

From the  $k_2$  and  $k_3$  values at three temperatures, we Materials. The solvent, acetonitrile, was of HPLC grade determined the activation parameters,  $\Delta H^{\neq}$  and  $\Delta S^{\neq}$ , for (Aldrich), and was further distilled over phosphorus pentoxide. The benzylamine nucleophiles, of GR grade (Aldrich), were used without further purification. Preparations of deuterated benzylamines were as described previously.14 The analysis (NMR and GC-mass spectrometry) of the deuterated benzylamines showed more than a 99% deuterium content, so no corrections to kinetic effects for incomplete deuterium content were made.15

each pathways. The results in Table 5 indicate that the  $\Delta H^{\neq}$ and  $-\Delta S^{\neq}$  values are relatively small for the  $k_2$  processes, but the  $\Delta H^{\neq}$  values are very small and the  $-\Delta S^{\neq}$  values are fairly large for the  $k_3$  processes. These are in good accord with the trends found for the corresponding activation parameters for the uncatalyzed and catalyzed stepwise breakdown processes of the tetrahedral intermediate,  $T^{\pm}$ , in

Table 4. Kinetic isotope effects on the second-  $(k_2)$  and the third-order rate constants  $(k_3)$  for the reactions of p-nitrophenyl N-(Y)phenylcarbamates with deuterated X-benzylamines [XC6H4CH2NH2(D2)] in acetonitrile at 25.0 °C

Х	Y	$k_{2(H)} (\mathrm{dm^3  mol^{-1}})$	$k_{2(D)} (\mathrm{dm^3  mol^{-1}})$	$k_{ m H}/k_{ m D}$
p-CH <sub>3</sub>	p-CH <sub>3</sub>	$0.958 \pm 0.007^{a}$ 8.49 ± 0.06	$0.855 \pm 0.008$ 7.19 + 0.05	$1.12\pm0.03$ $1.18\pm0.02$
m-Cl m-Cl	<i>p</i> -CH <sub>3</sub> <i>m</i> -Cl	$0.112 \pm 0.004$ $2.29 \pm 0.02$	$0.102 \pm 0.004$ $2.01 \pm 0.04$	$1.10\pm0.02$ $1.10\pm0.05$ $1.14\pm0.04$
x	Y	$k_{3(\mathrm{H})} (\mathrm{dm^6  mol^{-2}  s^{-1}})$	$k_{3(D)} (\mathrm{dm^6  mol^{-2}  s^{-1}})$	$k_{\rm H}/k_{\rm D}$
<i>p</i> -CH <sub>3</sub> <i>p</i> -CH <sub>3</sub> <i>m</i> -Cl <i>m</i> -Cl	<i>p</i> -CH <sub>3</sub> <i>p</i> -Cl <i>p</i> -CH <sub>3</sub> <i>p</i> -Cl	$\begin{array}{c} 9.45 \pm 0.06^{a} \\ 32.3 \pm 0.8 \\ 1.28 \pm 0.04^{a} \\ 4.98 \pm 0.08 \end{array}$	$5.59 \pm 0.06 \\ 19.9 \pm 0.6 \\ 0.703 \pm 0.007 \\ 2.80 \pm 0.06$	$1.69 \pm 0.03$ $1.62 \pm 0.04$ $1.82 \pm 0.04$ $1.78 \pm 0.03$

<sup>a</sup> Standard deviation. <sup>b</sup> Standard error.

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Table 5. Activation parameters<sup>a</sup> for the reactions of *p*-nitrophenyl (*N*-(Y)phenylcarbamates with X-benzylamines in acetonitrile

X	Y	Reaction	$\Delta H^{\neq}$ (kcal mol <sup>-1</sup> )	$-\Delta S^{\neq}$ (cal mol <sup>-1</sup> K <sup>-1</sup> )
p-CH <sub>3</sub>	p-CH <sub>3</sub>	$k_2$	14.3	11
p-CH <sub>3</sub>	m-Cl	$k_2$	14.2	9
m-Cl	$p-CH_3$	$\bar{k_2}$	14.8	15
m-Cl	m-Cl	$k_2$	14.2	15
$p-CH_3$	$p-CH_3$	$k_3$	1.1	53
m-Cl	$p-CH_3$	$k_3$	1.4	53

<sup>a</sup> Calculated values at 25.0 °C.

Substrates. *p*-Nitrophenyl *N*-phenylcarbamate. A solution of *p*-nitrophenol (0·01 mol) in dry benzene (10 ml) was added to a solution of phenyl isocyanate (0·01 mol). A catalytic quantity (0·5 ml) of pyridine was added and the solution refluxed for 1 h. On evaporation of the solvent *in vacuo*, the carbamate precipitated and was recrystallized from chloroform–pentane. The other substituted phenyl *N*-phenylcarbamates were prepared in an analogous manner and recrystallized from chloroform–pentane. The substrates synthesized were confirmed by spectral and elemental analysis as follows.

*p***-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NHC(= O)OC<sub>6</sub>H<sub>4</sub>-***p***-NO<sub>2</sub>: m.p. 135–136 °C; δ<sub>H</sub> (CDCl<sub>3</sub>), 7·2–8·3 (8H, m, phenyl), 6·9 (1H, s, NH), 2·3 (3H, s, CH<sub>3</sub>); \nu\_{max} (KBr), 3400 (NH), 2800 (CH, aromatic), 1720 (C=O); m/z 272 (M<sup>+</sup>). Calc. for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>: C, 61·8; H, 4·4. Found: C, 61·8; H, 4·3%.** 

**C**<sub>6</sub>**H**<sub>5</sub>**NHC**(**=O**)**OC**<sub>6</sub>**H**<sub>4</sub>**-***p***-NO**<sub>2</sub>**:** m.p. 146–148 °C;  $\delta_{\rm H}$  (CDCl<sub>3</sub>), 7·2–8·3 (9H, m, phenyl), 6·8 (1H, s, NH);  $\nu_{\rm max}$  (KBr), 3400 (NH), 2800 (CH, aromatic), 1720 (C=O); *m/z* 258 (M<sup>+</sup>). Calc. for C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>: C, 60·5; H, 3·9. Found: C, 60·4; H, 3·8%.

*p***-ClC<sub>6</sub>H<sub>4</sub>NHC(=O)OC<sub>6</sub>H<sub>4</sub>-***p***-NO<sub>2</sub>: m.p. 111–112 °C; δ<sub>H</sub> (CDCl<sub>3</sub>), 7·2–8·3 (8H, m, phenyl), 6·9 (1H, s, NH); \nu\_{max} (KBr), 3400 (NH), 2800 (CH, aromatic), 1720 (C=O);** *m/z* **292 (M<sup>+</sup>). Calc. for C<sub>13</sub>H<sub>9</sub>N<sub>2</sub>O<sub>4</sub>Cl: C, 53·4; H, 3·1. Found: C, 53·3; H, 3·1%.** 

*m*-ClC<sub>6</sub>H<sub>4</sub>NHC(=O)OC<sub>6</sub>H<sub>4</sub>-*p*-NO<sub>2</sub>: m.p. 111–112 °C; δ<sub>H</sub> (CDCl<sub>3</sub>), 7·2–8·3 (8H, m, phenyl), 6·9 (1H, s, NH);  $\nu_{max}$ (KBr), 3400 (NH), 2800 (CH, aromatic), 1720 (C=O); *m*/*z* 292 (M<sup>+</sup>). Calc. for C<sub>13</sub>H<sub>9</sub>N<sub>2</sub>O<sub>4</sub>Cl: C, 53·4; H, 3·1. Found: C, 53·3; H, 3·1%.

**Deuterated** *p*-nitrophenyl *N*-phenyl carbamate  $[C_6H_5NDC(=O)OC_6H_4-p-NO_2]$ . DOC<sub>6</sub>H<sub>4</sub>-*p*-NO<sub>2</sub>: a solution of potassium hydroxide in methanol was added to a solution of *p*-nitrophenol. The reaction mixtures were kept for 2 h and the solvent, methanol, was removed. The salt, KOC<sub>6</sub>H<sub>4</sub>-*p*-NO<sub>2</sub>, was dissolved in excess D<sub>2</sub>O under a nitrogen atmosphere and left over 12 h at 25.0 °C. The solution was neutralized with DCl. The deuterated *p*-nitrophenol was extracted with dry diethyl ether and dried

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again over MgSO<sub>4</sub>. After expulsion of solvent, the analysis (GC–mass spectrometry) of dried deuterated p-nitrophenol had >99% deuterium content.

**C**<sub>6</sub>**H**<sub>5</sub>**NDC**(=**O**)**OC**<sub>6</sub>**H**<sub>4</sub>**-***p***-NO**<sub>2</sub>: a solution of deuterated *p*-nitrophenol (0·01 mol) in dry benzene (10 ml) was added to a solution of phenyl isocyanate (0·01 mol). A catalytic quantity (0·5 mol) of pyridine was added and the solution was refluxed for 1 h. On evaporation of the solvent *in vacuo*, the carbamate precipitated and was recrystallized from chloroform–pentane. The deuterated substrate synthesized was confirmed by spectral and mass spectrometric analysis as follows. **C**<sub>6</sub>**H**<sub>5</sub>**NDC**(=**O**)**C**C<sub>6</sub>**H**<sub>4</sub>**-***p*-**NO**<sub>2</sub>: m.p. 146–148 °C;  $\delta_{\rm H}$  (CDCl<sub>3</sub>), 7·2–8·3 (9H, m, phenyl);  $\nu_{\rm max}$  (KBr), 2800 (CH, aromatic), 2300 (ND), 1720 (C=O); *m*/*z* 259 (M<sup>+</sup>).

**Kinetic procedures.** Rates were measured conductimetrically in acetonitrile. The conductivity bridge used in this work was a laboratory-made computer aromatic A/D converter conductivity bridge. Pseudo-first-order rate constants,  $k_{obs}$ , were determined by the Guggenheim method<sup>16</sup> with a large excess of benzylamine; [carbamate-]= $2.0 \times 10^{-4}$  mol dm<sup>-3</sup> and [benzylamine=0.02-0.25 moldm<sup>-3</sup>. The rate constants  $k_2$  and  $k_3$  were obtained by plotting  $k_{obs}/$ [benzylamine] vs [benzylamine] and determining the intercept and slope of the straight line. The  $k_2$  and  $k_3$  values in Tables 1 and 2 are the averages of more than triplicate runs and were reproducible to within  $\pm 3\%$ .

**Product analysis.** *p*-Nitrophenyl *N*-phenylcarbamate was reacted with excess *p*-methylbenzyl amine with stirring for more than 15 half-lives at  $25.0 \text{ }^{\circ}\text{C}$  in acetonitrile and the products were isolated by evaporating the solvent under reduced pressure. The product mixture was subjected to column chromatography (silica gel, 20% ethyl acetate–*n*-hexane). Analysis of the product gave the following results.

**C**<sub>6</sub>**H**<sub>5</sub>**NHC**(=**O**)**NHCH**<sub>2</sub>**C**<sub>6</sub>**H**<sub>4</sub>-*p*-**CH**<sub>3</sub>: **R**<sub>F</sub>=0.33 (20% ethyl acetate–*n*-hexane); m.p. 182–184 °C;  $\delta_{\rm H}$ (CDCl<sub>3</sub>), 7·2–8·2 (9H, m, C<sub>6</sub>H<sub>5</sub>, C<sub>6</sub>H<sub>4</sub>), 6·9 (1H, s, NH), 4·2 (2H, d, CH<sub>2</sub>), 2·1 (3H, s, CH<sub>3</sub>);  $\nu_{\rm max}$  (KBr), 3220 (NH), 3050–3100(CH), 2950 (CH, aromatic), 1710 (C=O); *m/z* 285 (M<sup>+</sup>). Calc. for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O: C, 63·2; H, 5·6. Found: C, 63·1; H, 5·5%.

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