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Kinetics and mechanism of base-catalysed degradations of substituted aryl-*N*-hydroxycarbamates, their *N*-methyl and *N*-phenyl analogues

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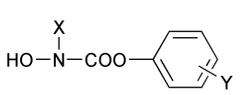
The kinetics and mechanism of the degradation reactions of substituted phenyl *N*-hydroxycarbamates and their *N*-methyl and *N*-phenyl analogues have been studied at pseudo-first-order reaction conditions in aqueous buffers and sodium hydroxide solutions at 20 °C and 60 °C and at $I = 1$ mol·l^{-1}. The dependence of log k_{obs} on pH for phenyl *N*-hydroxycarbamates at pH < 9 and pH > 13 is linear with the unit slope; at pH 10–12 log k_{obs} is pH independent. The Bronsted coefficient β_{lg} is about −1 (pH 7–13) and −1.53 (pH > 13) indicating that the degradation reaction of phenyl *N*-hydroxycarbamates follows an E1cB mechanism giving the corresponding phenol/phenolate and HO–N=C=O. The latter species undergoes further decomposition to give carbonate, nitrogen and ammonia as final products. In contrast to the phenyl *N*-hydroxycarbamates the *N*-methyl derivatives at pH 7–9 undergo degradation to the corresponding phenol/phenolate, carbonate and methylamine *via* a concerted mechanism (β_{lg} is about −0.75). The only exception is 4-nitrophenyl *N*-hydroxy-*N*-methylcarbamate in which the predominant break down pathway proceeds *via* the Smiles rearrangement to give sodium *N*-methyl-(4-nitrophenoxy)carbamate. At pH > 9 the reaction of *N*-hydroxy-*N*-methylcarbamates is kinetically complex: the dependence of absorbance on time is not exponential and it proceeds as a consecutive two-step reaction. *N*-Hydroxy-*N*-phenylcarbamate under the same conditions undergoes degradation to phenol, carbonate, aniline and azoxybenzene.

Introduction

Certain aryl *N*-hydroxycarbamic acids display biological activity[1] as fungicides, acaricides and ovicides. The presence of an ionisable hydroxyl group near the reactive carbonyl group in these substrates can induce intramolecular reactions, out of which only the Smiles rearrangement has been studied so far. 4-Nitrophenyl *N*-hydroxycarbamate undergoes the Smiles rearrangement under base-catalysed conditions.[2] Phenyl *N*-hydroxycarbamate, on the other hand does not undergo this rearrangement, but its hydrolysis has been shown to proceed at two orders of magnitude faster than that of phenyl *N*-methoxycarbamate.[3] The aim of this work was to carry out a detailed study of the mechanism of the base catalysed degradation of *N*-hydroxycarbamates (**1**–**3**). The structures investigated are shown in Fig. 1.



1: X = H
2: X = CH_3
3: X = C_6H_5

a: Y = H
b: Y = 4-CH_3
c: Y = 3-Cl
d: Y = 4-Cl
e: Y = 3-NO_2
f: Y = 4-NO_2
g: Y = 3,5-$(NO_2)_2$
h: Y = 3-NO_2-4-Cl

Fig. 1

Experimental

General preparation of aryl *N*-hydroxycarbamates and their *N*-methyl and *N*-phenyl analogues

A solution of substituted phenyl chloroformate (10 mmol) in ether (10 ml) was added within 30 min drop by drop with stirring and cooling at 5–10 °C into a suspension of substituted hydroxylamine hydrochloride (10 mmol), potassium carbonate (11 mmol) in ether (10 ml) and water (1 ml). Then the reaction mixture was stirred at room temperature for another 5 h. The separated ether phase was dried, the solvent was distilled off, and the evaporation residue was recrystallised from a suitable solvent.

Phenyl-*N*-hydroxycarbamate (1a)

(51%), Mp 106 −106.5 °C (*n*-heptane–ether), (lit.[4] 105–107 °C). IR (nujol), ν_{max}/cm^{-1}: 3305s, 1287s (NH), 3128wb (OH), 1690s (C=O), 1600w, 1492m, 689m ($C_{Ar}C_{Ar}$), 1207s, 1170m, 1028w (C–O), 795m (CH). NMR δ_H(360 MHz; $CDCl_3$; Me_4Si): 6.40 (1H, br s, OH), 7.14 (2H, d, J 7.8, H-2,6), 7.23 (1H, t, J 7.2, H-4), 7.38 (2H, t, J = 8.0, H-3,5), 7.50 (1H, br s, NH). δ_C(90.6 MHz; $CDCl_3$; Me_4Si): 121.7 (C-2,6), 125.3 (C-4), 129.5 (C-3,5), 150.9 (C-1), 155.7 (C=O). UV λ_{max} (MeOH)/nm, (ε/m^2 mol^{-1}): 204 (893), 260 (29).

4-Methylphenyl-*N*-hydroxycarbamate (1b)

(36%), Mp 99–100.5 °C (*n*-heptane), lit.[5] 99 °C. IR (nujol), ν_{max}/cm^{-1}: 3262sb, 1285sh, 1272s (NH), 3325sb (OH), 1700vs (C=O), 1506s ($C_{Ar}C_{Ar}$), 1378w, 827m (CH), 1208s, 1173w, 1020m (C–O). NMR δ_H(360 MHz; $CDCl_3$; Me_4Si): 1.70 (1H, br s, NH), 2.33 (3H, s, CH_3), 7.00 (2H, d, J 8.8, H-2,6), 7.16 (2H, d, J 9.0, H-3,5), 7.55 (1H, br s, OH). δ_C(90.6 MHz; $CDCl_3$; Me_4Si): 21.3 (CH_3), 121.2 (C-2,6), 130.2 (C-3,5), 135.9 (C-4), 148.3 (C-1), 157.7 (C=O). UV λ_{max} (MeOH)/nm, (ε/m^2 mol^{-1}): 202 (898), 266 (52), 272 (48).

3-Chlorophenyl-*N*-hydroxycarbamate (1c)

(42%), Mp 99.5–101 °C (*n*-heptane), IR (nujol), ν_{max}/cm^{-1}: 3318s, 1285s (NH), 3168sb (OH), 1746vs, 1717vs (C=O), 1598m, 1593m, 675s ($C_{Ar}C_{Ar}$), 1224s, 1167w (C–O), 1071w (C_{Ar}–Cl), 868m, 793m (CH). NMR δ_H(360 MHz; $CDCl_3$; Me_4Si): 7.06 (1H, d, J 9.1, H-2), 7.18–7.23 (2H, m, H-4,6), 7.28–7.37 (1H, d, J 9.0, H-3). δ_C(90.6 MHz; $CDCl_3$; Me_4Si):120.7 (C-2), 121.8 (C-6), 125.3 (C-4), 129.6 (C-3), 133.4 (C-5), 151.6 (C-1), 155.7 (C-7). Elemental analysis: found C, 44.76; H, 3.16;

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N, 7.57. Calc. for $C_7H_6NO_3Cl$: C, 44.82; H, 3.22; N, 7.45%. UV λ_{max} (MeOH)/nm, (ε/m^2 mol^{-1}): 204 (1417), 266 (39), 273 (34).

4-Chlorophenyl-*N*-hydroxycarbamate (1d)

(45%), Mp 140–142 °C (*n*-heptane), lit.[5] 127 °C. IR (nujol), ν_{max}/cm^{-1}: 3320vs, 1285m (NH), 1745vs (C=O), 1480s, 1492m ($C_{Ar}C_{Ar}$), 1220s, 1171w (C–O), 1082s (C_{Ar}–Cl), 847s (CH). NMR δ_H(360 MHz; $CDCl_3$; Me_4Si): 7.20 (2H, d, J = 7.0, H-2,6), 7.48 (2H, d, J 7.0, H-3,5), 9.19 (1H, br s, NH), 10.45 (1H, br s, OH). δ_C(90.6 MHz; $CDCl_3$; Me_4Si): 123.6 (C-2,6), 129.3 (C-3,5), 129.4 (C-4), 149.6 (C-1), 155.2 (C=O). Elemental analysis: found C, 44.82; H, 3.22; N, 7.45. Calc. for $C_7H_6NO_3Cl$: C, 45.32; H, 2.93; N, 7.64%. UV λ_{max} (MeOH)/nm, (ε/m^2 mol^{-1}): 201 (883), 220 (1095), 269 (49), 275 (43).

3-Nitrophenyl-*N*-hydroxycarbamate (1e)

(22%), Mp 132–134 °C (xylene), lit.[5] 130.5 °C. IR (nujol), ν_{max}/cm^{-1}: 3378w, 1278m (NH), 3280mb, 3120w (OH), 1749vs, 1728vs, 1702s (C=O), 1616m, 1596m, 685w ($C_{Ar}C_{Ar}$), 1520sh, 1510s, 1358s (NO_2), 1215s, 1160m, 1020m (C–O), 869m (CH). NMR δ_H(360 MHz; $CDCl_3$; Me_4Si): 5.15 (1H, br s, NH), 7.58 (2H, m, H-2,3), 8.06 (1H, m, H-6), 8.12 (1H, td, J 8.0, H-4). δ_C(90.6 MHz; $CDCl_3$; Me_4Si):116.6 (C-6), 120.1 (C-4), 128.5 (C-2), 130.7 (C-3), 148.3 (C-5), 151.1 (C-1), 154.5 (C=O). UV λ_{max} (MeOH)/nm, (ε/m^2 mol^{-1}): 205 (1600), 259 (745).

4-Nitrophenyl-*N*-hydroxycarbamate (1f)

(33%), Mp 137–139.5 °C (xylene), lit.[6] 122–123 °C. IR (nujol), ν_{max}/cm^{-1}: 3400w, 3378w, 1280m (NH), 3280wb, 3180wb (OH), 1730vs, 1728vs, 1705s (C=O), 1618m, 1598m ($C_{Ar}C_{Ar}$), 1518vs, 1510vs, 1360s (NO_2), 1217s, 1170m (C–O). NMR δ_H(360 MHz; DMSO-d_6; Me_4Si): 6.98 (2H, m, H-2), 8.16 (1H, m, H-3), 8.42 (1H, br s, OH), 8.88 (1H, br s, NH). δ_C(90.6 MHz; DMSO-d_6; Me_4Si): 115.8 (C-2,6), 126.2 (C-3,5), 139.6 (C-4), 163.9 (C=O), 164.1 (C-1). Elemental analysis: found C, 42.43; H, 3.05; N, 14.14; Calc. for $C_7H_6N_2O_5$: C, 42.82; H, 2.76; N, 13.71%. UV λ_{max} (MeOH)/nm, (ε/m^2 mol^{-1}): 202 (1107), 274 (855).

Phenyl-*N*-hydroxy-*N*-methylcarbamate (2a)

(92%), Mp 60–61.5 °C (*n*-heptane), lit.[7] 58–60 °C. IR (nujol), ν_{max}/cm^{-1}: 3128sb (OH), 1732vs, 1697vs (C=O), 1595m, 1488s, 691m ($C_{Ar}C_{Ar}$), 1198s, 1170s, 1037m (C–O), 758s (CH). NMR δ_H(360 MHz; $CDCl_3$; Me_4Si): 3.28 (3H, s, NCH_3), 7.08 (2H, d, J 8.0, (H-2,6), 7.17 (1H, t, J 8.0, H-4), 7.34 (2H, t, J 8.0, H-3,5), 8.15 (1H, br s, OH). δ_C(90.6 MHz; $CDCl_3$; Me_4Si): 38.4 (NCH_3), 121.6 (C-2,6), 125.9 (C-4), 129.5 (C-3,5), 150.9 (C-1), 156.2 (C=O). UV λ_{max} (MeOH)/nm, (ε/m^2 mol^{-1}): 204 (1029), 260 (29).

4-Methylphenyl-*N*-hydroxy-*N*-methylcarbamate (2b)

(46%), Mp 64–65.5 °C (*n*-heptane–toluene), lit.[8] 35–36 °C IR (nujol), ν_{max}/cm^{-1}: 3300sb (OH), 1680vs (C=O), 1510m (C_{Ar}-C_{Ar}), 1385vs, 810m (CH), 1190s, 1170w, 1020m (C–O). NMR δ_H(360 MHz; $CDCl_3$; Me_4Si): 2.31 (3H, s, $ArCH_3$), 3.27 (3H, s, NCH_3); 6.96 (2H, d, J 8.0 (H-2,6), 7.13 (2H, d, J 8.0, (H-3,5), 8.1 (1H, br s, OH). δ_C(90.6 MHz; $CDCl_3$; Me_4Si): 21.0 ($ArCH_3$), 38.4 (NCH_3), 121.3 (C-2,6), 130.1 (C-3,5), 135.6 (C-4), 148.5 (C-1); 156.5 (C=O). UV λ_{max} (MeOH)/nm, (ε/m^2 mol^{-1}): 203 (1150), 266 (52), 272 (47).

3-Chlorophenyl-*N*-hydroxy-*N*-methylcarbamate (2c)

(53%), Mp 92.5–94 °C (*n*-heptane), IR (nujol), ν_{max}/cm^{-1}: 3205sb (OH); 1738vs, 1698vs (C=O); 1595s, 678m ($C_{Ar}C_{Ar}$); 1214s, 1151s (C–O); 1071m (C_{Ar}–Cl); 875m, 782m (CH). NMR δ_H(360 MHz; $CDCl_3$; Me_4Si): 3.33 (3H, s, NCH_3), 7.02 (1H, t, J8.0, H-2), 7.15 (1H, m,. H-6), 7.20 (1H, d, J 8.0, H-4), 7.28 (1H, m, H-3), 7.35–7.95 (1H, br s, OH). δ_C(90.6 MHz; $CDCl_3$; Me_4Si): 38.4 (NCH_3), 120.0 (C-2), 122.3 (C-6), 126.2 (C-4), 130.3 (C-3), 134.8 (C-5), 151.5 (C-1), 155.6 (C=O). Elemental analysis: found C, 47.82; H, 4.05; N, 6.92. Calc. for $C_8H_8ClNO_3$: C, 47.66; H, 4.00; N, 6.95%. UV λ_{max} (MeOH)/nm, (ε/m^2 mol^{-1}): 203 (1603), 266 (39).

4-Chlorophenyl-*N*-hydroxy-*N*-methylcarbamate (2d)

(55%), Mp 121–123 °C (*n*-heptane), lit.[10] 114–115 °C. IR (nujol), ν_{max}/cm^{-1}: 3208vsb, 3150sh (OH), 1728vs, 1961vs (C=O), 1428m, 809s (CH), 1222s, 1173m, 1020m, (C–O), 1089m (C_{Ar}–Cl). NMR δ_H(360 MHz; $CDCl_3$; Me_4Si): 3.32 (3H, s, NCH_3), 7.04 (2H, d, J 9.0, H-2,6), 7.31 (2H, d, J 9.0, H-3,5), 7.4–8.2 (1H, br s, OH). δ_C(90.6 MHz; $CDCl_3$; Me_4Si): 38.3 (NCH_3), 123.0 (C-2,6), 129.7 (C-3,5), 131.4 (C-4), 149.5 (C-1), 155.8 (C=O). Elemental analysis: found C, 47.81; H, 4.11; N, 6.84. Calc. for $C_8H_8ClNO_3$: C, 47.66; H, 4.00; N, 6.95%. UV λ_{max} (MeOH)/nm, (ε/m^2 mol^{-1}): 203 (1107), 220 (1245), 268 (47).

3-Nitrophenyl-*N*-hydroxy-*N*-methylcarbamate (2e)

(57%), Mp 150–151 °C (*n*-heptane, xylene). IR (nujol), ν_{max}/cm^{-1}: 3260mb, 3122w (OH); 1732vs, 1708s (C=O), 1617m, 1598m, 689w ($C_{Ar}C_{Ar}$), 1528vs, 1520vs, 1350vs (NO_2), 1265m (N–H), 1229s, 1162m, 1025m (C–O), 869m (CH). NMR δ_H(360 MHz; $CDCl_3$; Me_4Si): 3.40 (3H, s, NCH_3), 8.05 (1H, t, J 2.1, H-2), 8.15 (1H, m, H-4), 7.74 (1H, t, J 8.2, H-5), 7.68 (1H, m, H-6). δ_C(90.6 MHz; $CDCl_3$; Me_4Si): 38.6 (NCH_3), 116.9 (C-6), 120.3 (C-4), 128.6 (C-2), 130.7 (C-3), 148.2 (C-5), 151.3 (C-1), 153.8 (C=O). Elemental analysis: found C, 45.15; H, 3.62; N, 13.11. Calc. for $C_8H_8N_2O_5$: C, 45.29; H, 3.80; N, 13.20%. UV λ_{max} (MeOH)/nm, (ε/m^2 mol^{-1}): 208 (1789), 259 (794).

4-Nitrophenyl-*N*-hydroxy-*N*-methylcarbamate (2f)

(76%), Mp 113–114 °C (xylene). IR (nujol), ν_{max}/cm^{-1}: 3250sb, 3125w (OH); 1735vs, 1708s (C=O); 1618m, 1598m ($C_{Ar}C_{Ar}$), 1528vs, 1521vs, 1351s (NO_2), 1230vs, 1164m, 1027m (C–O), 749m (CH). NMR δ_H(360 MHz; $CDCl_3$; Me_4Si): 3.38 (3H, s, NCH_3), 7.31 (2H, d, J 9.0, H-2,6), 7.75 (2H, d, J 9.0, H-3,5). δ_C(90.6 MHz; $CDCl_3$; Me_4Si): 38.6 (NCH_3), 113.6 (C-2,6), 124.1 (C-3,5), 125.8 (C-4), 140.7 (C-1), 165.9 (C=O). Elemental analysis: found C, 45.37; H, 3.65; N, 12.95. Calc. for $C_8H_8N_2O_5$: C, 45.29; H, 3.80; N, 13.20%. UV λ_{max} (MeOH)/nm, (ε/m^2 mol^{-1}): 204 (1279), 286 (771).

3,5-Dinitrophenyl-*N*-hydroxy-*N*-methylcarbamate (2g)

(11%), Mp 121–122.5 °C, (*n*-hexane–toluene). NMR δ_H(360 MHz; $CDCl_3$; Me_4Si): 3.47 3H, s, NCH_3), 6.4–7.1 (1H, br s, OH), 8.44 (2H, d, J 1.5, H-2,6), 8.96 (1H, t, J 1.6, H-4). Elemental analysis: found C, 37.34; H, 2.84; N, 16.47. Calc. for $C_8H_7N_3O_7$: C, 37.36; H, 2.75; N, 16.34%. UV λ_{max} (MeOH)/nm, (ε/m^2 mol^{-1}): 205 (1119), 268 (752).

4-Chloro-3-nitro-*N*-hydroxy-*N*-methylcarbamate (2h)

(35%) Mp 159–161 °C (*n*-heptane–xylene). NMR δ_H(360 MHz; $CDCl_3$; Me_4Si): 3.38 (3H, s, NCH_3), 7.57 (1H, dd, J 8.8, J 2.7, H-6), 7.84 (1H, d, J 8.8, H-5), 8.02 (1H, d, J 2.7, H-2). Elemental analysis: found C, 39.14; H, 2.84; Cl, 14.47; N, 11.15. Calc. for $C_8H_7ClN_2O_5$: C, 38.96; H, 2.86; Cl 14.38; N, 11.36%. UV λ_{max} (MeOH)/nm, (ε/m^2 mol^{-1}): 261 (815).

Phenyl-*N*-phenyl-*N*-hydroxycarbamate (3a)

(46%) Mp 127.5–128.5 °C (*n*-heptane–toluene), lit.[5] mp 124 °C. IR (nujol), ν_{max}/cm^{-1}: 3270sb, 3158w (OH), 1680vs (C=O), 1595m, 1497m, 692m, 689m ($C_{Ar}C_{Ar}$), 1198s, 1160m (C–O), 752s, 741s (CH). NMR δ_H(360 MHz; $CDCl_3$; Me_4Si): 7.18 (2H, m, Ar), 7.19–7.24 (2H, m, Ar), 7.31–7.38 (4H, m, Ar), 7.52 (4H, m, Ar), 7.75 (1H, br s, OH). δ_C(90.6 MHz; $CDCl_3$; Me_4Si): 121.6, 122.6, 126.2, 126.7, 129.0, 129.7, 140.3, 150.9, 153.8

(C=O). UV λ_{max} (MeOH)/nm, (ε/m^2 mol^{-1}): 205 (1610), 1437 (27).

Phenyl-*N*-methyl-*N*-methoxycarbamate

(61%) n_D^{20} = 1.5072 lit.,[3] n_D^{20} = 1.5069. IR (nujol), ν_{max}/cm^{-1}: 3070wb ($C_{Ar}H$), 2944w, 2820w, 1441m, 1374s, 750s (CH), 1750vs, 1730vs (C=O), 1594m, 690m ($C_{Ar}C_{Ar}$), 1212s, 1168m, 1030m (C–O). NMR δ_H(360 MHz; $CDCl_3$; Me_4Si): 3.17 (3H, s, NCH_3), 3.68 (3H, s, OCH_3), 7.08–7.15 (3H, m, H-2,4,6), 7.29 (1H, t, *J* 11.0, H-3,5). δ_C(90.6 MHz; $CDCl_3$; Me_4Si): 35.2 (NCH_3), 61.3 (OCH_3), 121.3 (C-2,6), 125.3 (C-4), 129.0 (C-3,5), 150.8 (C-1), 154.8 (C=O). UV λ_{max} (MeOH)/nm, (ε/m^2 mol^{-1}): 205 (1110), 259 (27).

***N*-methyl-*O*-(4-nitrophenyl)hydroxylamine**

Carbamate **2f** (0.15g, 1.4 mmol) was dissolved at room temperature in 0.1 M NaOH (30 ml). After 20 min the solution was acidified by conc. HCl (pH ≈ 2) and after 10 min treated with 5% aqueous NaOH (pH 12). Then the mixture was extracted into ether (3 ×15 ml), dried and evaporated. The residue (0.09g, 71%) was crystallised from toluene. Mp 127–129 °C. NMR δ_H(360 MHz; $CDCl_3$; Me_4Si): 3.36 (3H, s, NCH_3), 7.21 (2H, d, *J* 9.0, H-3,5), 8.24 (2H, d, *J* 9.0, H-4,6). Elemental analysis: found C, 49.74; H, 4.84; N, 16.41. Calc. for $C_7H_8N_2O_3$: C, 50.00; H, 4.80; N, 16.66%. UV λ_{max} (MeOH)/nm, (ε/m^2 mol^{-1}): 204 (230), 228 (681), 311 (1099). Hydrochloride mp 114–117 °C (decomp.).

Methods

The chromatographic measurements were carried out on a Varian HPLC, Model 5000 using Separon SGX C18 in 60% aqueous methanol. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker AMX 360 apparatus at 296 K. The chemical shifts are reported in ppm relative to TMS as an internal standard, and the coupling constants *J* are given in Hz. The IR spectra were recorded in Nujol or in a film on Perkin Elmer 684 and Data Station 3600 spectrometers. Mass spectra were recorded on Platform Micromass quadrupole mass spectrometer equipped with ESI and APCI with a column Separon SGX C18 in 60% aqueous methanol. The masses of the gaseous mixtures were measured on GC-MS-QP5050 with a Carboxene-1006 column of 30 cm length and 0.53 mm ID. UV-VIS spectra were measured on a Hewlett-Packard 8453 Diode Array apparatus. The pH values were determined with the use of an MV 870 instrument (VEB Pröcitronic) with a combination of glass electrode and silver electrode calibrated with standard aqueous buffers. The ionisation constants K_a of carbamates **1**–**3** were determined by spectral methods or from kinetic data or taken from the literature.[2]

Identification of degradation products of *N*-hydroxycarbamates 1a–3a

Procedure A. 1a (10 mmol) was suspended in water (5 ml) and covered with a layer of *n*-heptane in a sealed vessel equipped with an electromagnetic stirrer and a tube connected to an eudiometer. The vessel was kept at 60 °C and 1 M NaOH (10 ml) was injected *via* a septum into the suspension, and the aqueous phase was stirred for 60 min. During this period, the evolved gas was measured in the eudiometer. A sample of the gas was analysed by MS to determine the presence of nitrogen (*m*/*z* = 28). After mixing the aqueous phase with solid sodium hydroxide and heating the reaction mixture, ammonia gas evolved. The same procedure was adopted in the case of hydroxylamine hydrochloride and the potassium *N*-hydroxycarbamate freshly prepared according to Voigt.[9]

Procedure B. A sample of **1a** (10 mmol) was hydrolysed by stirring in a solution of 1 M NaOH (30 ml) at 60 °C. After 50 min, the mixture was cooled to 25 °C and a solution of 10% aqueous HCl was injected till pH 1–3. The gaseous products which contained carbon dioxide were bubbled into a solution of barium hydroxide to generate insoluble barium carbonate. Alternatively, the liberated gaseous products were carried in a stream of nitrogen through a tube packed with magnesium perchlorate (p.a.,0.8–1.5 mm, Merck) into a small column packed with sodium hydroxide on asbestos (0.8–1.6 mm, Merck). The carbon dioxide was determined from the mass increase of the column. The mass increase from **1a** was 97.5% of the theoretical value. The percentage of CO_2 in a similarly processed mixture of carbamates **2a** and **3a** was 85.7 and 96.0%, respectively.

Procedure C. A sample of **1a** (or **1e**, **2a** and **3a** respectively) (10 mmol) was submitted to hydrolysis under the same conditions as described in *Procedure B*. The cooled mixture was acidified with conc. HCl, extracted into ether (2 × 25 ml) and the extract was analysed by HPLC. The phenol concentration was quantified relative to a solution. The recovery of phenol was 91.0, 96.9, and 93.3% for **1a**, **2a**, and **3a**, respectively. Carbamate **1e** was submitted to the same procedure in phosphate buffer (pH 7.05) at 60 °C over 10 h. The yield of 3-nitrophenol was 94.4%.

Procedure D. Solutions of carbamates **1a**, **2a**, **3a** (10 mmol) in 1 M NaOH (5 ml) were submitted to partial hydrolysis at room temperature for 10 min, and then the pH was adjusted at 9 by addition of acetic acid. The same pH value was also adjusted in the hydrolysis products from **1a**, **2a**and **3a** obtained by *Procedure C*. Then the individual solutions were mixed with acetic anhydride (10 mmol), stirred at room temperature for 10 min, and finally mixed with a 3% aqueous solution of ferric chloride (1 ml), and the colour monitored. An analogous procedure was also applied to potassium *N*-hydroxycarbamate freshly prepared according to Voigt.[9] The colour of individual mixtures was compared with solutions of ferric complexes of acethydroxamic acids formed from the same molar amounts of hydroxylamine hydrochloride, or *N*-methyl- or *N*-phenylhydroxylamine hydrochloride and acetic anhydride in the presence of phenol.

Procedure E. The ^{13}C NMR spectra of the reaction mixture obtained by dissolving **1a** (10 mmol) in 10% NaOD (3 ml) in D_2O were measured at 30 min intervals at 20 °C. The decrease in the peak at 155.9 ppm (C=O) of the carbamate and the increase of the new peak at 165.9 ppm was monitored. The intensity of the latter peak increased after adding potassium carbonate to the reaction mixture. A similar procedure was also applied to study the course of decarboxylation of the hydroxycarbamate ion which is formed from **2a** and **3a** or potassium *N*-hydroxycarbamate.

Procedure F. Carbamate **3a** (1 g) was dissolved in 1 M NaOH (50 ml), and the mixture was stirred under nitrogen at room temperature for three weeks. The solution was washed with chloroform (3 × 30 ml) and the aqueous solution acidified with hydrochloric acid to pH 1 and extracted into ether. Both extracts were submitted to chromatographic analysis. The chloroform extract was concentrated and the products separated on silica gel using chloroform as the eluent. The major product was azoxybenzene (0.21 g, 75%); mp 33–35 °C. MS-HPLC (*m*/*z* = 198). The formation of this product was observed as early as after 24 h. In the chloroform extract, aniline was identified by GC-MS (*m*/*z* = 93) and phenol (0.345 g, 86%) was identified (GC-MS, *m*/*z* = 94) in the ether extract.

Kinetic experiments

For the kinetic analyses of carbamate hydrolysis the following buffers were used: phosphate, borax, carbonate, 2-amino-2-(hydroxymethyl)propan-1,3-diol; sodium hydroxide solutions

were used for pH above 12. The ionic strength was adjusted to I = 1.0 by addition of potassium chloride. The pH values of the resultant solution were measured by means of a combined electrode GK 2401 B, using a PHM-93 (Radiometer-Copenhagen) pH-meter at 25 °C. The pH values at 60 °C were determined on the same pH-meter calibrated at the respective temperature with the IUPAC standards with known pH-temperature dependences.[10] The ionic strength of 1 M NaOH and stronger solutions was unadjusted, and their basicity was taken from the literature.[11] The carbamate degradation reaction rates were followed spectrophotometrically, using a UV-VIS spectrometer HP 8453 (Hewlett-Packard) and quartz cells at constant temperature (thermostat). Very slow reactions (with half-lives below 1 h) were followed with a UV-VIS M 40 apparatus (Carl Zeiss). Solutions of the carbamates in methanol or dioxane were injected into the cell to a final concentration of 10^{-4}–10^{-5} M. Absorbance changes were followed at the wavelength corresponding to the absorption maximum of the liberated phenol/phenolate. These measurements were not perturbed by subsequent reactions, as the products of these reactions do not absorb at the wavelengths used, and there were no other reactions involving phenol/phenolate. The parameters A and k_{obs} were optimised by the method of non-linear regression using Eqn. (1):

$$A - A_0 = (A_\infty - A_0)\,(1 - e^{k_{obs}}) \qquad (1)$$

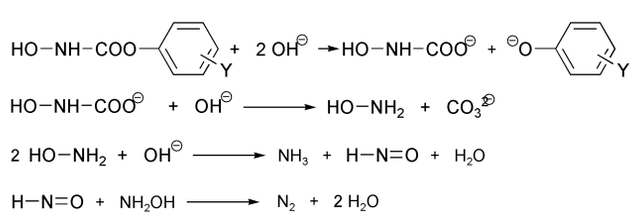
where A, A_0, and A_∞ are absorbances at time t, at the beginning, and at the end of the reaction, respectively.

Results and discussion

Substituted phenyl *N*-hydroxycarbamates **1a**–**f** and **3a** are stable crystalline solids. Their *N*-methyl analogues **2a**–**2f** are unstable substances slowly decomposing at 25 °C. In contrast to the substituted phenyl carbamates or *N*-methoxycarbamates, all *N*-hydroxycarbamates **1a**–**3a** are much more soluble in water as a consequence of the hydroxyl group.

Mechanism of base-catalysed degradation of substituted phenyl *N*-hydroxycarbamates

Carbamates **1a**–**e** are hydrolysed above pH 7 and generate the corresponding phenol or phenolate and the *N*-hydroxycarbamate almost quantitatively (see *Procedure C* and Scheme 1). An exception is the 4-nitro derivative **1f**, which at pH 12–13 generates *N*-(4-nitrophenoxy)carbamate, which is formed as a result of a rearrangement as described earlier.[2,12]



Scheme 1

N-Hydroxycarbamate could not be detected because it is rapidly decarboxylated to hydroxylamine and carbonate (Scheme 1), in contrast to *N*-aryl carbamates, *N*-alkyl carbamates and *N*-alkoxycarbamates,[3,13] which are relatively stable in basic media. After complete conversion of carbamate **1a** to the phenolate ion, hydroxylamine could not be detected. The formation of phenolate ion was accompanied by liberation of nitrogen from the reaction mixture and (after addition of further sodium hydroxide) by liberation of ammonia (Scheme 1). In a separate experiment the decomposition of hydroxylamine was monitored in 1 M aqueous NaOH at 60 °C, giving gaseous nitrogen and ammonia. Also the potassium *N*-hydroxycarbamate gives the same mixture of products (see *Procedure A*). The formation of nitrogen from hydroxylamine is about eight times (81% conversion) slower than the formation of phenolate from carbamate **1a**. The disproportionation of hydroxylamine in aqueous basic media was studied earlier by Luňák and Vepřek-Šiška.[14] The authors claim that hydroxylamine is decomposed in 1 M NaOH to ammonia and nitroxyl, which produces nitrogen by reaction with the remaining non-reacted hydroxylamine. At pH 7 they also found N_2O.

The base-catalysed decomposition of carbamates **1a**–**e** to substituted phenols and *N*-hydroxycarbamate proceeds kinetically as a pseudo-first-order reaction. The dependences of log k_{obs} on pH or log [OH^-] are presented in Fig. 2.

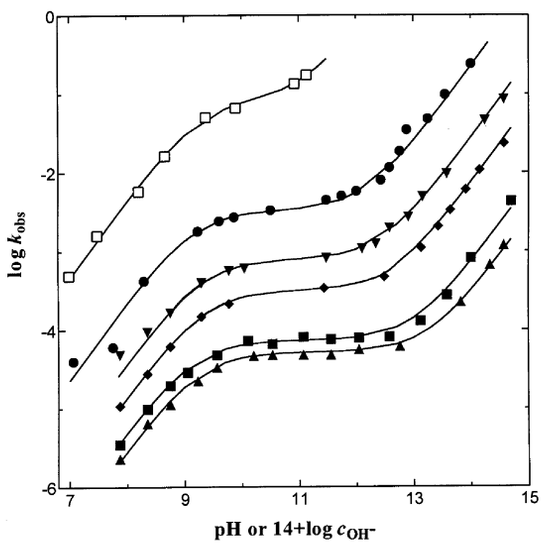


Fig. 2 Dependence of log k_{obs} of degradation of substituted phenyl *N*-hydroxycarbamates **1a**(■), **1b**(▲), **1c**(▼), **1d**(◆), **1e**(●) and **1f**(□) on pH or 14 + log c_{OH^-} at 25 °C. The curves correspond to Eqn. (5).

The dependence shown can generally be expressed by kinetic Eqn (2):[15,16]

$$k_{obs} = \frac{a[OH^-] + c[OH^-]^2}{1 + b[OH^-]} \qquad (2)$$

where a, b and c are coefficients of the rate equation. The first linear dependence in Fig. 2 with slope 1 and the transition to plateau with slope 0 are defined by the equation $k_{obs} = a[OH^-]/(1+b[OH^-])$. At low concentrations of hydroxyl ions, when $b[OH^-] << 1$, the value of k_{obs} is directly proportional to the concentration of hydroxyl ions, *i.e.* $k_{obs} = a[OH^-]$. At high concentrations of hydroxyl ions, when $b[OH^-] >> 1$, it is $k_{obs} = k_d' = a/b$, hence the reaction rate is independent of hydroxyl ion concentration. In Table 1, the value of constant k_{OH}^1 is given by experimentally determined coefficient a, and the value of constant k_d' is given by the ratio a/b.

The hydrolysis of carbamates can proceed either by an attack of hydroxyl ion on the carbonyl group with concomitant cleavage of the C–OAr bond (concerted mechanism) or by cleavage of a phenolate ion from the conjugate base of carbamate **1** in the rate-limiting step (E1cB) (Scheme 2).

k_c is the rate constant for the concerted reaction, k_d is the rate constant for the decomposition of the carbamate **1** anion. The reaction mechanism can be determined on the basis of the Brønsted dependence of log k_{OH}^1 or log k_d' from Table 1 on the change in pK_a^P of the leaving phenol (Eqns 3, 4).

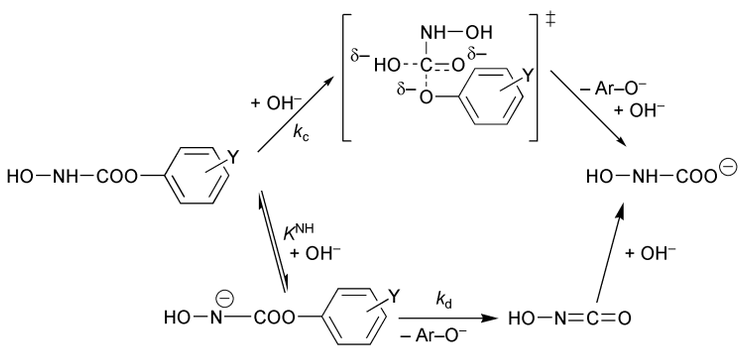
$$\frac{d(\log k_d')}{d(pK_a^p)} = (\beta_{lg})_{k_d'} \qquad (3)$$

$$\frac{d(\log k_{OH}^1)}{d(pK_a^p)} = (\beta_{lg})_{k_{OH}^1} \qquad (4)$$

Table 1 Kinetic data of degradation of carbamates **1a**–**3f**, **2a**–**h** and **3a** at 25 or 60 °C

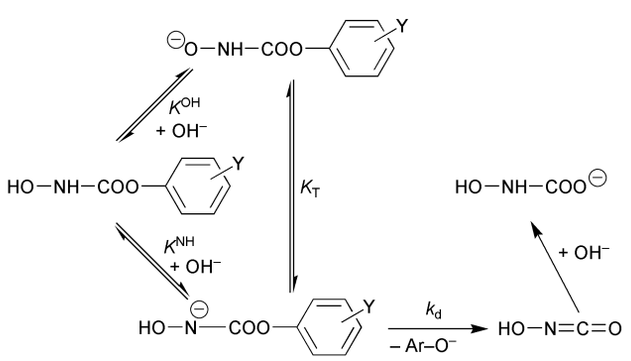
	$(10^5 \cdot K_1)^a$	$(pK_a)^a$	$(10^4 \cdot k_d')^b$	$(k_{OH}^1)^c$	$(10^3 \cdot k_{OH}^2)^c$	$(pK_a^p)^d$
1a	5.25 ± 0.8	9.28 ± 0.14	0.73 ± 0.04	5.13 ± 0.33	1.51 ± 0.08	9.99
1b	4.90 ± 0.9	9.31 ± 0.06	0.52 ± 0.03	2.95 ± 0.15	0.71 ± 0.05	10.25
1c	6.20 ± 0.7	9.21 ± 0.07	6.12 ± 0.33	38.1 ± 2.65	23.4 ± 0.15	9.08
1d	5.62 ± 0.9	9.25 ± 0.08	3.15 ± 0.15	14.1 ± 0.62	6.45 ± 0.25	9.42
1e	6.46 ± 0.6	9.19 ± 0.06	32.9 ± 1.77	230 ± 20.4	173 ± 11.7	8.38
1f[e]	7.59 ± 1.2	~9.1 ± 0.1	~850 ± 50	~4500	~45	7.16
2a[f]	—	9.29 ± 0.02[i]	—	11.7 ± 0.75	—	9.99
2b[f]	—	9.36 ± 0.05[i]	—	10.7 ± 0.64	—	10.30
2c[f]	—	9.16 ± 0.02[i]	—	45.1 ± 3.21	—	9.08
2d[f]	—	9.23 ± 0.02[i]	—	22.9 ± 1.77	—	9.42
2e[f]	—	9.04 ± 0.04[i]	—	258 ± 16.5	—	8.38
2f	71 ± 9	8.85 ± 0.03[i]	—	2187 ± 110	—	7.16
2g[f]	—	—	—	4467 ± 167	—	6.70[g]
2h[f]	—	—	—	758 ± 48.6	—	7.75[h]
3a[f]	72 ± 0.1	8.86 ± 0.06[i]	—	11.6 ± 0.31	—	9.99

[a] $K_a = K_1 \cdot K_W$; K_1 is defined in Eqn. (4) and its value is determined from kinetic data. [b] [s^{-1}]. [c] [$dm^3.mol^{-1}.s^{-1}$]; k_{OH}^2 is defined in Eqn.(6). [d] pK_a of the corresponding substituted phenol, taken from ref. 17. [e] Taken from ref. 2. [f] Measured at 60 °C. [g] Taken from ref. 18. [h] Taken from ref. 19. [i] Determined by spectral methods.



Scheme 2

For an E1cB reaction of this type β_{lg} is about −1 (refs. 20, 21). For a concerted mechanism, the β_{lg} values vary from −0.4 to −0.6, exceptionally[22] to −0.8. The calculated values are = −0.99 and = −0.93. That means that the hydrolysis of carbamates **1** proceeds by the E1cB mechanism (Scheme 3).



Scheme 3

In this case, the constants k_{obs} are defined by Eqn (5):

$$k_{obs} = \frac{k_d K^{NH}[OH^-]}{1 + K_1[OH^-]} = \frac{k_d' K_1[OH^-]}{1 + K_1[OH^-]} \quad \Rightarrow \quad k_d' = \frac{k_d K^{NH}}{K_1} \qquad (5)$$

where $k_{OH}^1 = k_d' \cdot K_1$ and $K_1 = K^{NH} + K^{OH}$.

The equilibrium constants K_1 and rate constants k_d' are experimentally determined constants and were calculated from Eqn. (5) by the non-linear regression method. K^{NH}, K^{OH} and k_d cannot be experimentally determined.

In order to roughly estimate the extent to which the proton is removed from N–H and O–H groups, we adopted the value of the ρ constant of ionisation of substituted carbamates **1** to the first degree (ρ = 0.13) and that of ionisation of substituted phenyl *N*-methoxycarbamates, which possess only one acidic proton N–H (ρ = 0.83).[3] The large difference between the two constants is due also to the fact that during the dissociation of the N–H bond, the negative charge is nearer to the substituent. We suppose that in carbamate **1** the O–H bond is predominantly cleaved, K_T is much higher than 1 and the value of k_d is substantially greater than k_d'.

The value $(\beta_{1g})_{k_{OH^2}} = -1.53$ found from the dependence of log k_{OH}^2 *vs.* pK_a^p corresponds to decomposition of the dianion also according to the E1cB mechanism (Scheme 4).

The values of rate constants k_{obs} in the measured range of hydroxyl ion concentration in Fig. 2 obey Eqn. (6):

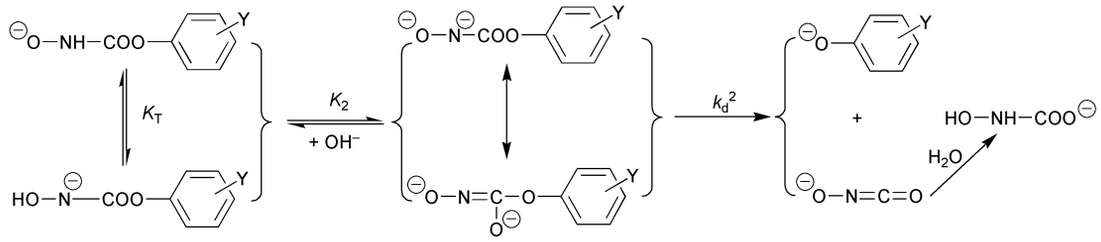
$$k_{obs} = \frac{k_d' K_1[OH^-] + k_d^2 K_1 K_2[OH^-]^2}{1 + K_1[OH^-]} \qquad (6)$$

At a high concentration of hydroxyl ions $K_1[OH^-] \gg 1$, and Eqn. (6) is simplified to Eqn. (7):

$$k_{obs} = k_d' + k_d^2 K_2[OH^-] \qquad (7)$$

where $k_d^2 K_2 = k_{OH}^2$ (Table 1).

The high negative value (−1.53) is caused by the fact that the substituent effect on $(\beta_{1g})_{k_{OH^2}}$ comes from the effects on both k_d^2 and K_2 in a similar way as that on $(\beta_{1g})_{k_{OH'}}$, but the effect on K_2 is much higher, because predominantly the N–H bond is broken. As the dependence of k_{obs} *vs.* log [OH^-] was linear in



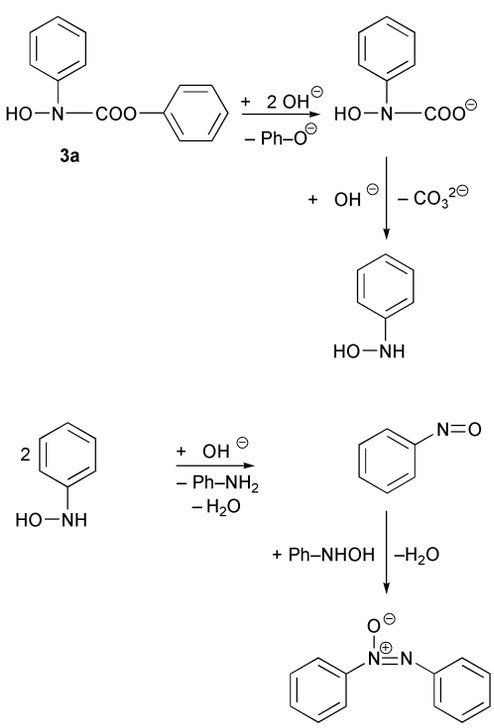
Scheme 4

the whole range measured (with the slope equal to 1), it was not possible to determine the values of K_2 and k_d^2 from experimental values.

Mechanism of base-catalysed degradation of phenyl *N*-hydroxy-*N*-methylcarbamates and of phenyl *N*-hydroxy-*N*-phenylcarbamates

The degradation products of substituted phenyl *N*-methylcarbamates **2a**–**2e**, **2g**, **2h** in aqueous bases are the corresponding phenols, methylamine, and carbonate. The qualitative test with Fe^{3+} did not prove the presence of *N*-methylhydroxylamine, even in the initial phase of the hydrolysis. In a separate experiment, *N*-methylhydroxylammonium chloride itself gave methylamine at the conditions of hydrolysis. Kjellin[23] reported that hydrolysis of *N*-methylhydroxylamine in aqueous sodium hydroxide produces ammonia, methylamine, and formate.

After base-catalysed degradation of carbamate **3a**, phenol, carbonate, azoxybenzene and aniline were detected in the reaction mixture (Scheme 5).



Scheme 5

It was also found that phenylhydroxylamine disproportionated in aqueous sodium hydroxide solution to aniline and azoxybenzene (Scheme 5). The formation of these products from phenylhydroxylamine under similar conditions was described by Bamberger and Brady.[24] Boyland and Nery[25] heated benzyl *N*-hydroxy-*N*-phenylcarbamate in sodium hydroxide solution and identified nitrosobenzene and phenylhydroxylamine. The pH dependence of log k_{obs} of carbamates **2a**–**h** at pH <8.5 is linear with the slope 1 (Fig. 3).

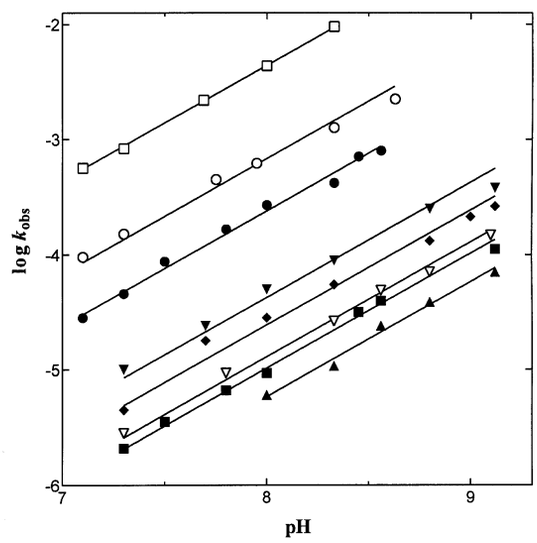
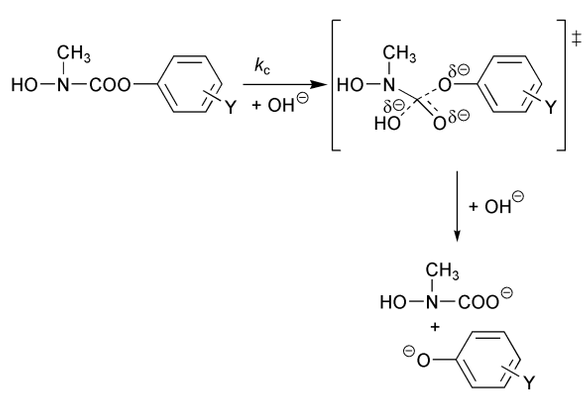


Fig. 3 Dependence of log k_{obs} of hydrolysis of substituted phenyl *N*-hydroxy-*N*-phenylcarbamates **2a**(■), **2b**(▲), **2c**(▼), **2d**(◆), **2e**(●), **2g**(□) **2h**(○) and phenyl *N*-hydroxy-*N*-phenylcarbamate **3a**(▽) on pH at 60 °C.

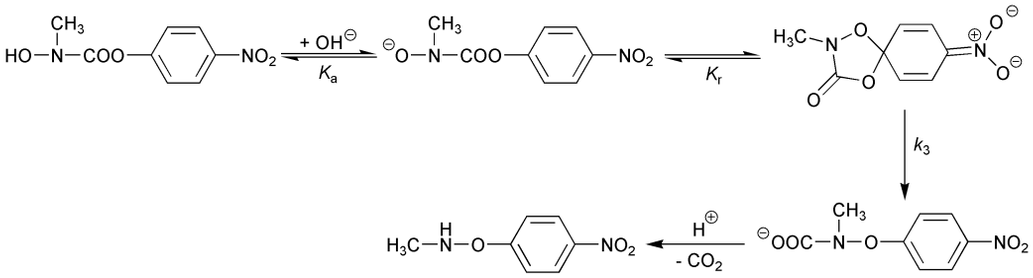
The Brønsted coefficient β_{lg} calculated from the log k_{OH}^1 values for the carbamates **2a**–**e** was −0.75. This corresponds to hydrolysis by a concerted mechanism (Scheme 6).



Scheme 6

In the case of addition–elimination mechanisms the addition of hydroxide ions to generate a tetrahedral intermediate is generally the rate limiting step because OH^- is a poor leaving group compared with Ar–O^-. Accordingly the Brønsted coefficient β_{lg} for this reaction varies[26] from 0.1 to 0.3.

In this pH range, carbamates **2** are present in their neutral form, hence the reaction rate $v = k_c.[\mathbf{2}][OH^-]$, and $k_{OH}^1 = k_c$ is the rate of formation of substituted phenol and *N*-hydroxy-*N*-methylcarbamate at 25 °C (except for **2f**). The 4-nitro derivative **2f** provides a mixture of *N*-hydroxy-*N*-methyl carbamate and 4-nitrophenol besides *N*-methyl-*N*-(4-nitrophenoxy)-carbamate (Scheme 7) in a ratio of 2 : 98. The major product of hydrolysis of **2f** after decarboxylation (during acidification) is *N*-methyl-*O*-(4-nitrophenyl)hydroxylamine similar to the **1f** derivative.[12]



Scheme 7

The value of the k_{OH}^{1} constant for the rearrangement of carbamate **2f** at 25 °C is almost one order of magnitude higher than the k_{OH}^{1} for the degradation of the 3-nitro derivative **2e** at 60 °C, but comparable with k_{OH}^{1} for derivative **1f**, which predominantly reacts by a E1cB mechanism (Fig. 4).

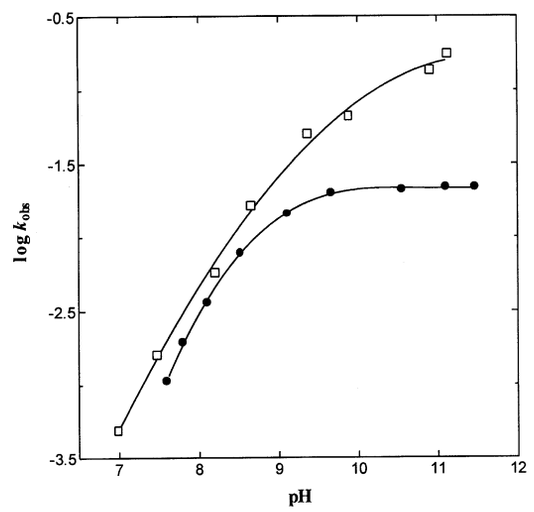


Fig. 4 The pH dependence of log k_{obs} of degradation and rearrangement of carbamates **1f**(□) and **2f**(●) at 25 °C.

At pH 8.5–9, the slope value of dependence of log k_{obs} *vs.* pH for carbamates **2** decreases, because their dissociation is increasingly important. At pH ≈ 10, the pH dependence of log k_{obs} should be linear and independent of pH, because the concentration of substrate is inversely proportional to the concentration of OH^- ions, hence the product [**2**]·[OH^-] is constant. Measuring the degradation rate of compounds **2a**–**e** and **2g** in carbonate buffers at pH 9.5, it was found that the absorbance–time dependence is no longer exponential, as two consecutive reactions are taking place. Their rates were determined from Eqn. (8)[27,28]

$$A_t - A_\infty = M \cdot e^{-k_f} + N \cdot e^{-k_s} \qquad (8)$$

where k_f and k_s are rate constants of the faster and slower steps, respectively.

The dependences of the rate constants log k_s and log k_f on the Hammett substituent constants σ are presented in Fig. 5.

The values of the reaction constants, $\rho_f = 0.65 \pm 0.17$ and $\rho_s = 1.09 \pm 0.14$, show a large scattering, which is due to the small difference between the two rate constants, and hence a relatively large error in their determination.[29] So far we have no explanation for this degradation course.

At pH > 9 the degradation is complex and we could not determine the values pK_a of carbamates **2** from the reaction kinetics. However, these values were determined by spectral method at 25 °C and were used for comparison with carbamates **1**. Although carbamates **2** only have one acidic proton, which is bound to oxygen, the ρ constant is about 0.32. This value is almost 3 times as large as that of carbamates **1**, where partial splitting of the N–H bond also takes place (the ρ constant of

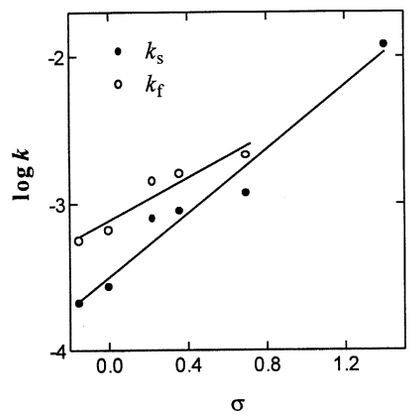


Fig. 5 Dependences of rate constants log k_s (•) and log k_f (○) on the Hammett σ constants for base-catalysed degradation of carbamates **2a**–**e** and **2g** at pH 9.5 at 60 °C.

N–H bond splitting is higher than that of O–H bond splitting). The lower ρ constant of carbamates **1** is obviously due to the strong hydrogen bond between a water molecule and N–H group of the neutral carbamate **1**, which stabilises the neutral substrate, whereas in its conjugate *O*-base the analogous bond is almost negligible. Electron-withdrawing substituents X in **1** stabilize the hydrogen bonding to the N–H bond, and ionisation of O–H in the molecule H–ON(H ··· OH_2)$COOC_6H_4X$ is diminished. In carbamates **2** H–ON(CH_3)$COOC_6H_4X$ the analogous ionisation is not affected by hydrogen bonding, and thus the ρ value is higher than that of carbamates **1**. A similar large effect on ionisation was observed when hydrogen was replaced by the methyl group in *N*-acetylthioureas:[30] CH_3-CONHC(=S)$NHCH_3$, pK_a = 16.6 and $CH_3CON(CH_3)C(=S)$-$NHCH_3$, pK_a = 14.5.

Fig. 6 gives the pH dependence of log k_{obs} for **1a** and its

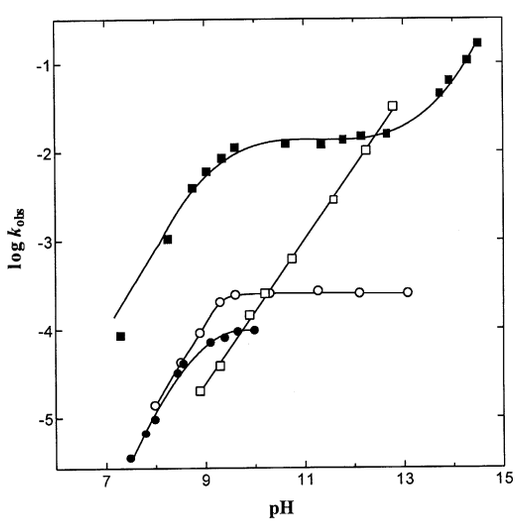


Fig. 6 Dependence of rate of base-catalysed degradation on pH values for carbamates **1a**(■), **2a**(□), phenyl *N*-methoxycarbamate **4a**(○) and phenyl *N*-methoxy-*N*-methylcarbamate **5a**(●) at 60 °C.

O-methyl derivative (**4a**), and for **2a** and its *O*-methyl derivative (**5a**). Carbamates **2a** and **5a** (ref. 3) are hydrolysed at almost identical rates at pH < 10 at 60 °C. On the other hand, carbamate **1a** is hydrolysed almost two orders of magnitude faster than **4a** in spite of the fact that carbamate **1a** undergoes predominant O–H bond splitting, which gives a non-reactive conjugate base. Both carbamates (**1a** and **4a**) react by a E1cB mechanism. In the base formed by dissociation of the N–H bond in carbamate **1a**, the hydrogen bond between the adjacent OH and water is very weak. The value $\beta_{lg} = -0.92$ suggests a transition state in which the splitting of the C–O bond has advanced to a large extent. The structure of the transition state thus resembles that of a complex formed from phenolate ion and the acid HO–N=C=O, which forms a strong hydrogen bond with a water molecule. In this way, water can act as a base catalyst facilitating the degradation of carbamate **1a**.

Acknowledgements

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