Aminolysis of sulfamate esters in chloroform—nonlinear kinetics

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Aminolysis in chloroform of sulfamate esters $RNHSO_2OC_6H_4NO_2$-4 principally with a series of imidazoles gives good k_{obs} first-order rate constants under pseudo-first-order conditions. Plots of k_{obs} *vs.* [amine] display downward curvature leading to saturation and these plots can be fitted to the rate law $k_{obs} = K_m k^1[amine]/\{1 + K_m[amine]\}$ where K_m and k^1 are defined by eqn. (i). The Hammett ρ value for the

$$S + Amine \overset{K_m}{\rightleftharpoons} [S{\cdot}Amine] \xrightarrow[rds]{k^1} Products \qquad (i)$$

formation of the complex [S·Amine] is +1.64. Using data derived for the rate-determining step, the breakup of the intermediate is shown to be unimolecular with a ρ_{acyl} (substituents in the R part of S) of −1.78 consistent with an E1cB process. Steric effects of the bound-amine in the complex are negligible.

Sulfonyl and sulfonate transfer reactions under non-aqueous conditions generally involving aminolysis of sulfonyl halides or sulfonates have been widely reported.[1–4] Recently, sulfamoyl transfer reactions involving aminolysis of several sulfamate esters in chloroform and acetonitrile (Scheme 1) have been studied and an E2 type process is proposed for these reactions.[5]

$$\underset{\mathbf{1}}{RNHSO_2ONp} + R'NH_2 \longrightarrow {}^-ONp + RNHSO_2NHR'$$

$$Np = p\text{-}O_2NC_6H_4$$

Scheme 1

In our latest work on these aminolysis reactions we have found that a number of them display nonlinear kinetics in non-aqueous media and the findings are presented and discussed here.

Results and discussion

Product studies using spent kinetic solutions have shown[5] that in chloroform and acetonitrile reaction proceeds quantitatively as shown in Scheme 1. Some additional product studies are described in the Experimental.

Kinetic studies were carried out in the chosen organic solvent under pseudo-first-order conditions (at least ten-fold excess of amine). A first-order dependence on the ester concentration was established in chloroform at 37 °C with cyclopentylamine at 0.15 mol dm^{-3} by varying the concentration of **1**, R = Ph and **1**, R = H in the range 0.2–2.0 × 10^4 mol dm^{-3}. For **1**, R = Ph the variation in 10^4 k_{obs} s^{-1} over five determinations was 3.43 ± 0.05 and for **1**, R = H the variation over eight determinations was 6.77 ± 0.15.

Plots of k_{obs} *vs.* [amine] showed downward curvature for a set of imidazoles reacting with **1**, R = H (see Figs. 1 and 2). This saturation kinetic behaviour is most likely due to complex formation between substrate and amine in the first step of the reaction and this is followed by a second rate-determining step (rds). Nonlinear kinetics of this type have been treated in this way for the methylimidazole-catalyzed hydrolysis of some *p*-nitrophenyl carboxylate esters,[6a] the aminolysis in dimethyl sulfoxide (DMSO) of similar esters,[6b] and periodate oxidation.[7]

The situation may be represented as reaction (i). For such a

$$S + RNH_2 \overset{K_m}{\rightleftharpoons} [S{\cdot}RNH_2] \xrightarrow[rds]{k^1} products \qquad (i)$$

system[8] the observed rate constant is given by eqn. (1) and this

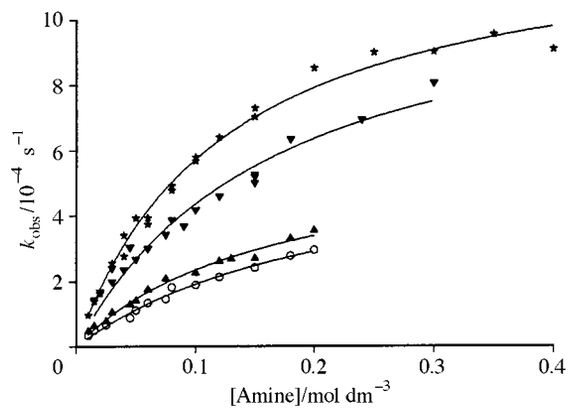


Fig. 1 Plots of k_{obs} *vs.* [amine] for reaction of 4-nitrophenyl sulfamate in chloroform at 37 °C for 2-isopropyl-(★), 1-methyl-(▼), 2-phenyl-(▲) and 4-phenyl-(○) imidazoles

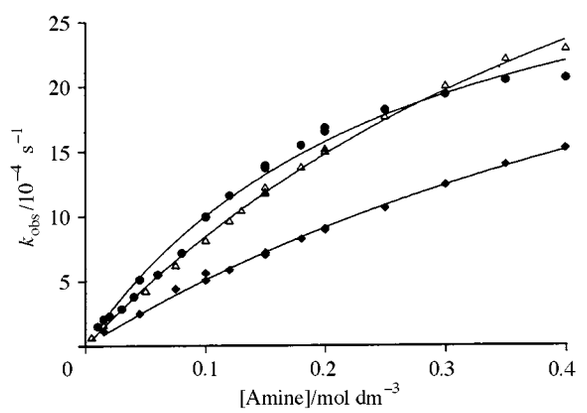


Fig. 2 Plots of k_{obs} *vs.* [amine] for reaction of 4-nitrophenyl sulfamate in chloroform at 37 °C for 2-methyl-(●), 4-methyl-(△) imidazoles and imidazole (◆)

$$k_{obs} = K_m k^1[RNH_2]/(1 + K_m[RNH_2]) \qquad (1)$$

may be rearranged to eqn. (2). Thus a 'double reciprocal' plot

$$1/k_{obs} = 1/K_m k^1[RNH_2] + 1/k^1 \qquad (2)$$

of $1/k_{obs}$ *vs.* $1/[RNH_2]$ should yield a straight line of slope $1/K_m k^1$ (mol dm^{-3} s) and an intercept of $1/k^1$(s).

The reactions in Table 1 for **1**, R = Ph, $PhCH_2$, Me and H all displayed downward curvature in plots of k_{obs} *vs.* [amine].

Table 1 Association constants (K_m) and rate constants (k^1) for reaction of 4-nitrophenyl *N*-phenyl-, *N*-benzyl-, *N*-methyl- and *N*-unsubstituted-sulfamates with imidazoles (X-Im) in chloroform at 37 °C

Substrate[a] (R in Scheme 1)	X	[X-Im]/10^{-2} mol dm^{-3}	K_m/mol^{-1} dm^3	±SE[b]	$k^1/10^{-4}$ s^{-1}	±(SE)[b]/10^{-4}	n[c]
Ph							
	2-Pr^i	2.0-10.0	76.2	5.6	2.04	0.05	9
	2-Me	2.0-10.0	41.1	1.7	2.87	0.14	7
	4-Me	1.5-17.0	45.1	1.9	2.96	0.30	11
	1-Me	4.0-20.0	13.5	1.4	4.58	0.27	12
	H	4.0-40.0	7.3	0.4	6.51	0.58	13
	2-Ph	0.6-20.0	16.7	1.7	2.90	0.09	20
	4-Ph	3.0-10.0	11.6	0.9	1.60	0.30	16
$PhCH_2$							
	2-Pr^i	5.0-20.0	6.3	0.5	7.43	0.63	7
	2-Me	2.0-20.0	22.0	1.1	2.07	0.10	5
	4-Me	1.0-15.0	9.6	1.3	5.71	0.57	11
	1-Me	4.0-20.0	4.9	0.6	6.79	0.48	12
	H	5.0-20.0	4.5	0.7	5.75	0.64	5
	2-Ph	5.0-20.0	4.3	0.5	4.11	0.45	11
	4-Ph	2.0-20.0	4.8	0.6	3.12	0.45	8
Me							
	2-Pr^i	2.0-20.0	10.4	0.47	5.18	0.47	8
	2-Me	2.0-10.0	9.87	0.12	6.00	0.05	5
	4-Me	3.0-20.0	9.4	0.24	4.76	0.53	9
	1-Me	3.0-20.0	10.7	0.43	3.83	0.23	6
	H	4.0-20.0	4.97	0.08	7.30	0.32	5
	2-Ph	4.0-20-0	7.79	0.31	3.01	0.29	9
	4-Ph[d]						
H							
	2-Pr^i	1.0-40.0	7.3	0.46	13.6	0.42	21
	2-Me	1.5-40.0	3.4	0.41	36.6	2.2	19
	4-Me	0.5-40.0	1.7	0.12	58.4	2.9	17
	1-Me	1.5-30.0	5.8	0.98	11.9	1.1	19
	H	1.5-40.0	1.3	0.13	44.2	3.2	16
	2-Ph	1.0-20.0	6.4	0.84	6.0	0.45	14
	4-Ph[d]	1.0-20.0	4.6	0.64	6.1	0.55	14

[a] 1×10^{-4} mol dm^{-3}. [b] Standard error. [c] No. of points. All correlation coefficients (r) were ⩾ 0.990. [d] Not determined.

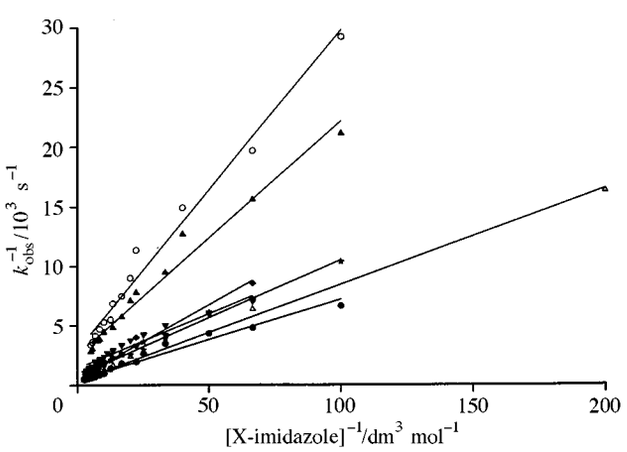


Fig. 3 Double reciprocal plots of k_{obs}^{-1} *vs.* [X-imidazole]$^{-1}$ for the reaction of 4-nitrophenyl sulfamate in chloroform at 37 °C with 4-phenyl-(○), 2-phenyl-(▲), 2-methyl-(●), 1-methyl-(▼), 4-methyl-(△), 2-isopropyl-(★) imidazoles and imidazole (◆)

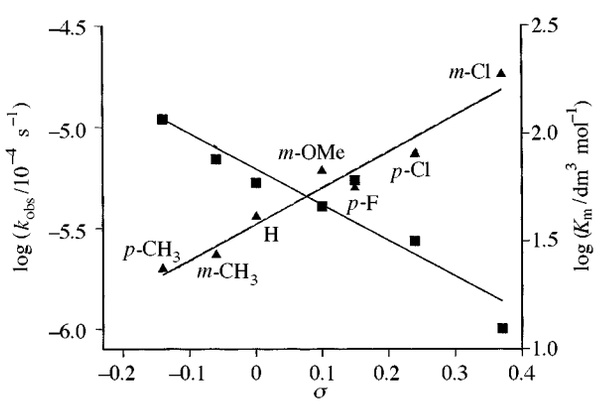


Fig. 4 Hammett plots for the aminolysis of 4-nitrophenyl *N*-X-phenylsulfamates with 4-methylimidazole in chloroform at 37 °C. Log K_m *vs.* σ (▲) and log k *vs.* σ (■).

All the data for **1**, R = H (Table 1, bottom section) have been plotted in Figs. 1 and 2 where the points are experimental but the curves are theoretical based on eqn. (1) above.

The K_m and k^1 values were either obtained by curve fitting the experimental data to eqn. (1) using the Biosoft FIG. P non-linear regression analysis program or from double reciprocal plots (see Fig. 3). The standard errors (SE values) in K_m or k^1 are given together with a correlation coefficient (r) indicating the quality of fit of the data to eqn. (1). Table 1 also contains the range of amine concentrations used and the number of points (n) in each plot. Some of the SE values for k^1 are quite large but despite duplicating/triplicating runs these could not be reduced.

All the data in Table 2 relate to the reaction of a set of substituted phenyl esters with 4-methylimidazole in chloroform. Using these data, two Hammett plots (Fig. 4) may be made. They correspond to log $K_m = 1.64\sigma + 1.61$ ($r = 0.977$) and log $k^1 = -1.78\sigma - 5.23$ ($r = 0.978$).

In Table 3 details of the activation data for six of the seven compounds in Table 2 are given. The use of K_m values in Arrhenius plots was unsatisfactory and the activation data were not obtainable for the initial association. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values given therefore relate to the rate-determining step

Table 2 Association constants (K_m) and rate constants (k') for reaction of 4-nitrophenyl *N*-X-phenylsulfamates[a] with 4-methylimidazole in chloroform at 37 °C

Substituent (X)	σ	[4-MeIm]/10^{-2} mol dm^{-3}	K_m/mol^{-1} dm^3	±SE[b]	$k^1/10^{-4}$ s^{-1}	±(SE)[b]/10^{-4}	*n*	*r*
4-Me	−0.14	1.0–20.0	27.3	4.6	4.11	0.21	8	0.993
3-Me	−0.06	0.1–20.0	23.6	4.1	6.58	0.35	13	0.986
H	0	0.1–17.0	41.2	2.0	3.17	0.04	14	0.998
3-MeO	0.10	0.1–20.0	68.4	8.2	2.41	0.07	13	0.993
4-F	0.15	0.1–12.0	55.8	6.1	3.27	0.11	11	0.995
4-Cl	0.24	0.1–12.5	80.2	11.5	1.63	0.06	11	0.988
3-Cl	0.37	0.1–20.0	187.7	23.6	1.01	0.03	11	0.986

[a] 1×10^{-4} mol dm^{-3}. [b] Standard error.

Table 3 Activation data for reactions of 4-nitrophenyl *N*-X-phenylsulfamates[a] in chloroform

Substituent (X)	*T*/K	*n*[b]	*r*[c]	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
4-Me	298–318	3	0.995	100 ± 7	17.5 ± 1.5
3-Me	294–318	4	0.998	95 ± 3	−3.4 ± 0.3
H	287–319	4	0.999	94 ± 3	−11 ± 1
4-F	294–318	4	0.997	98 ± 4	7 ± 1
4-Cl	294–318	4	0.999	98 ± 2	0.2 ± 0.02
3-Cl	294–318	4	0.998	114 ± 2	46 ± 3

[a] 1×10^{-4} mol dm^{-3}. Plots were made using k_{obs} values for different 4-methylimidazole concentrations and from those k^1 rate constants were computed for the various temperatures and used in the Arrhenius plots (see Fig. 5). [b] No. of points in Arrhenius plot. [c] Correlation for Arrhenius plot.

Table 4 Examination of steric effects in the reaction of 4-nitrophenyl *N*-phenyl-, *N*-methyl- and *N*-benzyl-sulfamates[a] in chloroform at 37 °C

Substrate	Amine	[Amine]/10^{-2} mol dm^{-3}	K_m/mol^{-1} dm^3	±SE[b]	$k^1/10^{-4}$ s^{-1}	±(SE)[b]/10^{-4}	*n*	*r*
Ph	Pyr[c]	0.25-20.0	7.14	1.1	2.95	0.25	17	0.992
	cyc-$C_5H_9NH_2$	0.10-15.0	6.21	1.4	7.00	1.1	7	0.995
	Bu^tNH_2	1.0-20.0	11.9	1.4	4.07	0.25	8	0.997
Me	Pyr[c]	1.0-20.0	3.65	2.08	0.20	0.56	16	0.993
	cyc-$C_5H_9NH_2$	1.5-15.0	4.34	4.51	0.41	0.58	5	0.998
$PhCH_2$	2-NH_2Pyr	0.3-20.0	6.59	2.5	2.36	0.47	6	0.978
	2,6-Me_2Pyr	2.0-20.0	5.57	3.6	2.57	0.91	5	0.995
	2,4,6-Me_3Pyr	1.0-20.0	6.29	1.3	2.48	0.28	6	0.995

[a] 1×10^{-4} mol dm^{-3}. [b] Standard error. [c] Pyr = pyridine.

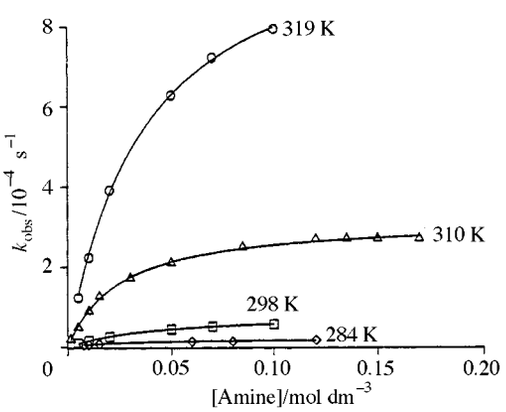


Fig. 5 Plots of k_{obs} *vs.* [4-methylimidazole] in chloroform at four temperatures. For reactions of **1**, R = Ph.

(k^1). Fig. 5 shows the k_{obs} *vs.* [amine] plots for 4-nitrophenyl *N*-phenylsulfamate at various temperatures. Each of these was analyzed to give k^1 values which were then used in the Arrhenius plots.

In Table 4 data are given which attempt to examine possible steric effects on the formation of the association complex (K_m) and its breakup (k^1). *tert*-Butylamine does not seem to exert a noticeable effect on either process though it does seem to bind more strongly than pyridine or cyclopentylamine. In the reactions with **1**, R = $PhCH_2$ some steric effect might be expected with the 2,6-dimethyl- and the 2,4,6-trimethyl-pyridines but no effect is observable either in the association with substrate or the decomposition of the complexes.

Plots of k_{obs} *vs.* [amine] showed downward curves (see Figs. 1 and 2 for example with **1**, R = H) for all the data in Table 1. This is referred to as rectangular hyperbolic dependence.[6a] Thus 'saturation' type kinetics are observed and the reaction is initially first order in amine and eventually zero order in amine.

Aminolysis in non-aqueous solvents of esters[9,10] and related carbonyl-containing substrates[11] often follows a rate law involving a second-order term in amine but we found no evidence for such a rate law in our present work. Thus, a second molecule of amine is not involved in the aminolysis of the sulfamate esters.

The possibility that the imidazoles or other amines used might be self-associating especially at the higher amine concentrations was also checked. Such self-aggregation of pyridines (conc. range 0.1–1.2 mol dm^{-3}) in water accounts for the downward curve in plots of observed rate constants in the reactions of 4-nitrophenyl phosphate with pyridines.[12] The association of *n*-butylamine in benzene, *n*-heptane and dichloroethane and the role of aggregates in its aminolysis reactions[13] and the association of diethylamine in acetone, acetonitrile and carbon tetrachloride[14] have been reported. In the case of imidazole in carbon tetrachloride, IR evidence indicated that oligomers form even in the range 2×10^{-4} to 4×10^{-3} mol dm^{-3}.[15]

In the present work a number of observations would indicate that the downward curved plots obtained cannot be ascribed to amine self-association: (1) the k_{obs} *vs.* [amine] plots give a much better fit to the rate law in eqn. (1) than to a 'dimerization'

model involving a square root term in amine;[6a] (2) the data in Tables 1 and 2 show that the association (formation) constants depend on the nature of the ester; (3) adherence to the Beer–Lambert law by the amines over the concentration ranges used in the kinetics was observed. Interestingly, and perhaps not surprisingly,[15] one case of association was encountered in this work. The k_{obs} *vs.* [4-methylimidazole] plot for the reaction of **1**, R = Ph in carbon tetrachloride at 37 °C showed downward curve but considerable scatter. A Beer–Lambert plot of absorbance of 4-methylimidazole (302 nm) *vs.* concentration began to deviate downwards above 0.1 mol dm^{-3} and in a ^1H NMR study with 4-methylimidazole over the range 0.01–0.2 mol dm^{-3} in CCl_4 the chemical shift data for the C-1 proton was found to fit a theoretical equation for dimerization quite well.

In short, the downward curves of the plots of k_{obs} *vs.* [amine] found throughout this work represent an example of saturation kinetics and are best treated using the rate law of eqn. (1). Application of this rate law allows one to obtain association or formation constants for the equilibrium formation of a noncovalent complex, $S{\cdot}RNH_2$ and the rate constants for the breakup of this complex in the rate determining step.

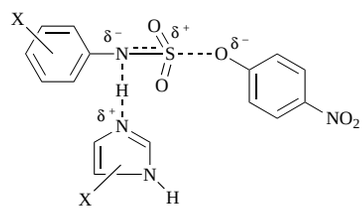
Equilibrium step (K_m)

From Table 1 it is clear that the binding ability of the four substrates decreases in the order **1**, R = Ph > **1**, R = Me = *ca.* **1**, R = $PhCH_2$ > **1**, R = H which is also the order of decreasing acidity[16a] of the bases $PhNH_2$ (4.87), $MeNH_2$ (10.66), $PhCH_2NH_2$ (9.34) and NH_3 (9.25). For the imidazoles the binding ability for a fixed substrate follows the approximate order: (pK_a values)[16b] 2-isopropyl (8.00) > 2.methyl (7.85) > 4-methyl (7.53) > 2-phenyl (6.40) and 4-phenyl (6.10). When attempts were made to correlate the K_m data with pK_a values or Hammett or Taft constants poor correlations were obtained probably because of the errors in the K_m values, which could be up to 16%, and the fact that it is difficult to choose σ or σ^* values for the various imidazoles. However, qualitatively it is seen that electron withdrawal in the substrate and electron donation in the amine facilitate formation of the intermediate complex; presumably the substrate and bound-amine exchange a proton. In Table 2 for a fixed imidazole, 4-methylimidazole, the strong effect of electron withdrawal in the substrate on K_m is clear and the data gave a ρ_{acyl} for the equilibrium of +1.64 (see Fig. 4). From Table 4 it is seen that the steric effects on the complex formation seem to be negligible and this would be expected if the main event is the transfer of a proton.

Rate-determining step (k^1)

The ability to access rate constants (k^1) for the rate-determining breakup of the substrate and amine-bound complex provides useful information on this crucial step of the overall reaction shown in Scheme 1. The breakup of the complex must be a unimolecular process since: (1) the kinetic analysis has shown that a second molecule of amine is not involved in this step, (2) the entropy data in Table 3 indicate that the process is dissociative in character rather than associative and (3) the effect of increasing pressure on some of these reactions, *e.g.* **1**, R = Ph in $CHCl_3$ at 37 °C using cyclopentylamine or cyclohexylamine (at 0.15 mol dm^{-3}) gives rise to behaviour typically associated with unimolecular reactions.[17]

Electron-donation in the amine speeds the decomposition of the complex and thus examination of Table 1 shows that in all cases the electron donating imidazoles, *e.g.* 2-isopropyl, 2-methylimidazoles, have larger k^1 values than the two phenylimidazoles, which are slightly electron-withdrawing. From the data in Table 2 a ρ value of −1.78 (see Fig. 4) is obtainable and thus electron-donation in the acyl portion of the substrate also facilitates reaction. This ρ value is identical with the value obtained for the E1cB reaction of the same esters in 50% acetonitrile–water[18] and much greater than the values obtained for the E2 type reaction of these esters in chloroform with 4-dimethylaminopyridine (ρ = −0.91).[5] Thus, an E1cB mechanism involving extensive S–O bond cleavage (Scheme 2)



Scheme 2

with the formation of an *N*-sulfonylamine, $ArN{=}SO_2$ is supported. Table 4 shows that there is little or no steric effect on k^1 from the amine bound in the complex and this amine may rapidly attack an incipient sulfonylamine following the slow step to form sulfamide product.

Experimental

Materials

Amines and reagents were obtained commercially and were distilled or recrystallized before use. The purification of chloroform was described previously.[5] The preparation of all the esters has been described previously[5,18] except for **1**, R = Me and this was prepared as described by Williams and Douglas,[19] mp 71.5–73 °C (lit.,[18] 70–72 °C), and C, H and N microanalytical data were within ±0.2%.

Products

Various product studies in $CHCl_3$ using HPLC and UV have been described previously[5] and they have shown that the reaction proceeds quantitatively as shown in Scheme 1. Some 'spent' (ten half lives) kinetic solutions from the reactions in Table 1 were compared with 4-nitrophenol standard solutions in chloroform and the absorbances of the 4-nitrophenol deviated by at most ±5%.

Kinetics

Rate constants, k_{obs} were measured as described in previous papers.[5,18] In quite a few cases it was possible to follow the rate by both the disappearance of substrate (λ_{max} 280 nm) or the appearance of 4-nitrophenol/4-nitrophenoxide (λ_{max} 320/400 nm). Good isosbestic points were obtained. The plots of k_{obs} *vs.* [amine] all passed through the origin; see for examples Figs. 1 and 2.

References

1 S. G. Sheiko, T. P. Kulishova, A. P. Korostylev and R. V. Vizgert, *Ukr. Khim. Zh.*, 1994, **60**, 652 and earlier papers.
2 O. Rogne, *J. Chem. Soc.*, *Perkin Trans. 2*, 1975, 1486; 1973, 823; 1972, 489, 472.
3 (*a*) V. A. Shatskaya, V. A. Savelova and L. M. Litvinenko, *Zh. Org. Khim.*, 1985, **21**, 875 and earlier papers; (*b*) L. M. Litvinenko, V. A. Savelova, T. N. Solomichenko, V. G. Zaslavskij and T. V. Ved, *Org. React.*, 1985, **22**, 162 and accompanying papers.
4 (*a*) I. Lee, C. H. Kang, P. S. Park and H. W. Lee, *Bull Korean Chem. Soc.*, 1991, **12**, 282 and references therein; (*b*) I. Lee, *Adv. Phys. Org. Chem.*, 1992, **27**, 57.
5 W. J. Spillane, G. Hogan, P. McGrath, J. King and C. Brack, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 2099.
6 (*a*) R. A. Gagliano, R. C. Knowlton and L. D. Byers, *J. Org. Chem.*, 1989, **54**, 5247; (*b*) J. Suh, Y. Kim, E. Lee and S. H. Chang, *Biorg. Chem.*, 1986, **14**, 33.
7 G. J. Buist, C. A. Bunton and W. C. P. Hipperson, *J. Chem. Soc. B*, 1971, 2128 and earlier references.
8 P. Zuman and R. C. Patel, in *Techniques in Organic Reaction Kinetics*, Wiley, New York, 1984, pp. 110–111.
9 M. J. Pfeiffer and S. B. Hanna, *J. Org. Chem.*, 1993, **58**, 735.

10 F. M. Menger and J. H. Smith, *J. Am. Chem. Soc.*, 1972, **94**, 3824; D. P. N. Satchell and L. I. Secemski, *J. Chem. Soc. B*, 1969, 130; O. B. Nagy, V. Reuliaux, N. Bertrand, A. van der Mensbrugghe, J. Leseul and J. B. Nagy, *Bull. Soc. Chim. Belg.*, 1985, **94**, 1055.
11 A. S. Shawali, A. Harhash, M. M. Sidky, H. M. Hassaneen and S. S. Elkaali, *J. Org. Chem.*, 1986, **51**, 3498; S. S. Alkaali and A. S. Shawali, *Can. J. Chem.*, 1992, **70**, 2515; M. Jedrzejczak, R. E. Motie and D. P. N. Satchell, *J. Chem. Soc.*, *Perkin Trans. 2*, 1993, 599.
12 A. J. Kirby and W. P. Jencks, *J. Am. Chem. Soc.*, 1965, **87**, 3209.
13 P. A. Berlin, R. P. Tiger, I. S. Filippova, M. A. Levina, M. N. Dzhaparidze, T. M. Kartvelishvili, R. D. Katsarova and S. G. Entelis, *Zh. Obshch. Khim.*, 1990, **60**, 2140; A. N. Zelenyuk, P. A. Berlin, R. P. Tiger and S. G. Entelis, *Kinet. Katal.*, 1994, **35**, 563.
14 P. B. Peshekhodov, A N. Petrov and G. A. Al'per, *Zh. Obshch. Khim.*, 1993, **63**, 1223.
15 D. M. W. Anderson, J. L. Duncan and F. J. C. Rossotti, *J. Chem. Soc.*, 1961, 2165.
16 (*a*) A. Albert and E. P. Serjeant, *The Determination of Ionization Constants*, 3rd edn., Chapman and Hall, New York, 1984; (*b*) D. D. Perrin, *Dissociation Constants of Organic Bases in Aqueous Solution*, Butterworth, London, 1965.
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18 W. J Spillane, G. Hogan and P. McGrath, *J. Phys. Org. Chem.*, 1995, **8**, 10.
19 A. Williams and K. T. Douglas, *J. Chem. Soc.*, *Perkin Trans. 2*, 1974, 1727.

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