JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 9, 152–158 (1996)

KINETIC AND EQUILIBRIUM STUDIES OF σ-ADDUCT FORMATION AND NUCLEOPHILIC SUBSTITUTION IN THE REACTIONS OF MORPHOLINE WITH 1,3,5-TRINITROBENZENE AND SOME PHENYL ARYL ETHERS IN DIMETHYL SULPHOXIDE

RACHEL A. CHAMBERLIN, MICHAEL R. CRAMPTON* AND IAN A. ROBOTHAM
Chemistry Department, Durham University, Durham DH1 3LE, UK

Reactions of morpholine in dimethyl sulphoxide at unsubstituted ring positions of 1,3,5-trinitrobenzene, and phenyl 2,4,6-trinitrophenyl ether, yield anionic σ-adducts via zwitterionic intermediates. Reactions at the 1-position of phenyl 2,4,6-trinitrophenyl ether, phenyl 2,4-dinitronaphthyl ether, and phenyl 2,4-dinitrophenyl ether result in substitution of the phenoxy groups. In both these reaction types proton-transfer is rate- limiting. Comparison of kinetic and equilibrium data with those for corresponding reactions of piperidine shows that rate constants for proton transfer are similar for the two amines, but equilibrium constants for zwitterion formation have lower values for morpholine, the less basic amine. Implications for base catalysis are discussed.

INTRODUCTION

Reactions of amines with aromatic nitro compounds in dimethyl sulphoxide (DMSO) may lead to the formation of stable anionic σ-adducts[1] or, when the substrate carries a suitable leaving group, to nucleophilic substitution.[2–4] An example,[5,6] of the former type is the reaction with 1,3,5-trinitrobenzene (**1**), where, as shown in Scheme 1, proton transfer from the zwitterionic intermediate (**2**), to base leads to the anionic adduct (**3**). The proton-transfer step, k_{Am}, may be rate limiting so that kinetic studies allow not only comparisons of nucleophilic reactivity of the amines but also of rate constants for proton transfer. Since the zwitterions (**2**), are stronger acids than the corresponding ammonium ions, the k_{Am} step is thermodynamically favoured.[7] However, the values of k_{Am} are considerably lower than the diffusion limit and decrease in the order *n*-butylamine (3×10^7 dm^3 mol^{-1} s^{-1}) > pyrrolidine ($1{\cdot}5 \times 10^6$ dm^3 mol^{-1} s^{-1}) > piperidine ($1{\cdot}4 \times 10^5$ dm^3 mol^{-1} s^{-1}). This decrease is thought to reflect increasing steric hindrance to the approach of the reagents.[5,6]

Many nucleophilic displacements in DMSO have been found to be subject to base catalysis,[1–4,8–10] as indicated in Scheme 2.

The base-catalysed pathway may, in an analogous fashion to that shown in Scheme 1, involve rate-limiting proton transfer from the zwitterionic intermediate to base, or it may involve general acid catalysis by BH^+ of leaving group departure. The latter, the SB–GA mechanism, has been shown to apply to substrates, such as alkyl ethers, carrying poor leaving groups.[11,12] However there is now strong evidence that for substrates, such as phenyl ethers and phenyl sulphides, carrying good leaving groups, base catalysis results from rate-limiting proton transfer from the zwitterions to base.[13,14] Sekiguchi *et al.*[15] have similarly produced evidence that base catalysis in the substitution reaction of *n*-butylamine with 1-pyrrolidino-2,4-dinitronaphthalene involves rate-limiting deprotonation of the zwitterionic intermediate.

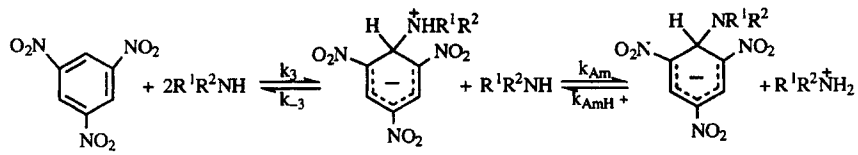
Data are available for reaction of **1** and of several phenyl aryl ethers with *n*-butylamine, pyrrolidine and piperidine.[5,6] We report here kinetic and equilibrium results for corresponding reactions with morpholine. This amine has similar steric requirements to piperidine but is a considerably weaker base. The pK_a values in water[16] are morpholine 8·36 and piperidine 11·06 and in acetonitrile[17] 16·62 and 18·92, respectively. Although precise data in DMSO are not available, morpholine is expected to be at least two pK units less basic than piperidine.

It has been noted previously that substitutions involving morpholine are generally more susceptible to base

* Author for correspondence.

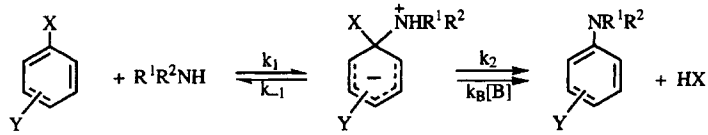
CCC 0894–3230/96/030152–07

Received 8 September 1995
Revised 5 December 1995



1 2 3

Scheme 1



Scheme 2

catalysis than corresponding reactions involving piperidine.[18,19] We hoped that a study by stopped-flow spectrophotometry would allow a detailed comparison of individual steps in the reactions and hence indicate the origin of this difference.

EXPERIMENTAL

1,3,5-Trinitrobenzene was a recrystallized commercial specimen, m.p. 123 °C. Phenyl ethers were available from previous work.[14] Morpholine and DMSO were the purest available commercial specimens. UV–visible spectra and kinetic measurements were made with Beckman Lambda 2 or Hi-Tech SF 3L stopped-flow spectrophotometers at 25 °C. Reported rate constants are the means of several determinations and are precise to ±5%. Rate constants were measured under first-order conditions. Hence for reactions in buffers (amine plus amine salt) the buffer components were in large excess over the substrate concentration (1×10^{-5}–5×10^{-5} mol dm^{-3}). For reactions with amine in the absence of salt a large excess of amine was used, sufficient in the case of σ-adduct-forming reactions to achieve >95% conversion into adduct at equilibrium. Under these, conditions equation (1) applies, and was used to calculate rate constants.

$$\ln\left(\frac{A\infty}{A\infty - A}\right) = k_{obs}t \qquad (1)$$

RESULTS AND DISCUSSION

1,3,5-Trinitrobenzene (1)

Reaction of **1** with morpholine in DMSO gave the adduct **3** ($R^1R^2 = CH_2CH_2OCH_2CH_2$) with λ_{max} 447 and 530 nm. The assumption that the zwitterionic form **2** may be treated as a steady-state intermediate leads to the following general rate expression:

$$k_{obs} = \frac{k_3 k_{Am}[Am]^2 + k_{-3}k_{AmH^+}[AmH^+]}{k_{-3} + k_{Am}[Am]} \qquad (2)$$

Values, given in Table 1, in the absence of added morpholinium salt show a precise dependence on the square of the amine concentration. This indicates that the proton-transfer step is rate determining, $k_{-3} \ll k_{Am}[Am]$. Hence equation (2) simplifies to

$$k_{obs} = K_3 k_{Am}[Am]^2 + k_{AmH^+}[AmH^+] \qquad (3)$$

where $K_3 = k_3/k_{-3}$.

Values calculated with $K_3k_{Am} = 8500$ dm^6 mol^{-2} s^{-1} and $k_{AmH^+} = 400$ dm^3 mol^{-1} s^{-1} gave excellent agreement with experimental values. Combination of these values gives a value for $K_{c,3}$, defined as

$$K_{c,3} = \frac{k_3}{k_{-3}}\frac{k_{Am}}{k_{AmH^+}} \qquad (4)$$

of 21 dm^3 mol^{-1}. Most data were obtained with salt concentrations of 0·01 mol dm^{-3}. Results in solutions where the total salt concentration was 0·1 mol dm^{-3} led to the values $K_3k_{Am} = 8500$ dm^6 mol^{-2} s^{-1} and $k_{AmH^+} = 250$ dm^3 mol^{-1} s^{-1}, yielding a slightly higher value for $K_{c,3}$ of 34 dm^3 mol^{-1}.

Measurements of the forward reaction were also made in the presence of DABCO, where the equation

$$k_{obs} = K_3[Am](k_{Am}[Am] + k_{DABCO}[DABCO]) \qquad (5)$$

applies. They yield a value for K_3k_{DABCO} of 5000 dm^6 mol^{-2} s^{-1}.

Phenyl 2,4,6-trinitrophenyl ether (4)

UV–visible measurements showed the presence of two reactions well separated in time, an initial reaction giving a species with λ_{max} 432 and 500 nm and a slower

Table 1. Kinetic data for reaction of **1** with morpholine in DMSO at 25 °C

[Morpholine]/mol dm^{-3}	[DABCO]/mol dm$_{-3}$	[Morpholinium perchlorate]mol dm^{-3}	k^{a}_{obs}/s^{-1}	k^{b}_{calc}/s^{-1}
0·02	—	—	3·4	3·4
0·03	—	—	7·9	7·7
0·04	—	—	14	14
0·05	—	—	20	21
0·06	—	—	30	31
0·08	—	—	55	54
0·10	—	—	81	85
0·02	0·05	—	8·0	8·4
0·02	0·10	—	13	13
0·02	0·15	—	18	18
0·02	0·20	—	24	23
0·01	—	0·01	4·7	4·8
0·02	—	0·01	7·8	7·4
0·03	—	0·01	12	12
0·04	—	0·01	18	18
0·05	—	0·01	25	25
0·06	—	0·01	34	34
0·10	—	0·01	82	89
0·02	—	0·01[c]	5·9	5·9[c]
0·02	—	0·02[c]	8·2	8·4[c]
0·02	—	0·03[c]	12	11[c]
0·04	—	0·01[c]	16	16[c]
0·04	—	0·02[c]	19	19[c]
0·04	—	0·03[c]	22	21[c]

[a] Measured as a colour-forming reaction at 445 nm with **1** at $2·5 \times 10^{-5}$ mol dm^{-3}.
[b] Calculated from equation (3) or (5) with $K_3k_{Am} = 8500$ dm^6 mol^{-2} s^{-1}, $K_3k_{DABCO} = 5000$ dm^6 mol^{-2} s^{-1} and $k_{AmH^+} = 400$ dm^3 mol^{-1} s^{-1}.
[c] Total salt concentration 0·1 mol dm^{-3} with tetraethylammonium perchlorate. Values calculated from equation (3) with $K_3k_{Am} = 8500$ dm^6 mol^{-2} s^{-1} and $k_{AmH^+} = 250$ dm^3 mol^{-1} s^{-1}.

reaction leading to a species whose spectrum was identical with that of the substitution product (**7**), in the same reaction medium. It is known[12-14] that amines show a kinetic preference for reaction at unsubstituted ring positions of 1-substituted-2,4,6-trinitrobenzenes, so that the rapid reaction is attributed to the formation of the 3-adduct **5**. Kinetic data for this reaction, given in Table 2, give an excellent fit with equation (3) with values $K_3k_{Am} = 2450$ dm^6 mol^{-2} s^{-1} and $k_{AmH^+} = 600$ dm^3 mol^{-1} s^{-1}. Substitution, leading to **7**, proceeded without the accumulation of the intermediate, **6**, on the reaction pathway. We have shown[14] that in the reaction of **4** with other aliphatic amines, leaving group expulsion, the k_4 step, is not rate limiting. On this assumption, the rate expression for product formation, allowing for rapid equilibration of **4** and **5**, is

$$k_{obs} = \frac{k_1k_{Am}[Am]^2}{k_{-1} + k_{Am}[Am]}\left(\frac{1}{1 + K_{c,3}[Am]^2/[AmH^+]}\right) \quad (6)$$

Our results indicate that the condition $k_{-1} \gg k_{Am}[Am]$ applies, so that equation (6) reduces to

$$k_{obs} = K_1k_{Am}[Am]^2\left(\frac{1}{1 + K_{c,3}[Am]^2/[AmH^+]}\right) \quad (7)$$

Values calculated with $K_1k_{Am} = 70$ dm^6 mol^{-2} s^{-1} were in good agreement with experimental data. It should be noted that, as in related systems,[20] the product, **7**, is in rapid equilibrium with the adduct formed by reaction with morpholine at the 3-position.

Phenyl 2,4-dinitronaphthyl ether (8)

A single process was observed, resulting in spectra identical with those of the expected reaction product in the same reaction medium. The substitution pathway will be analogous to that shown in Scheme 3 for **4** but without initial attack at the 3-position. Values of k_{obs}, given in Table 3, showed a dependence on the square of the amine concentration and catalysis by DABCO was observed. They give a good correlation with the equation

$$k_{obs} = K_1[Am](k_{Am}[Am] + k_{DABCO}[DABCO]) \quad (8)$$

with values $K_1k_{Am} = 11$ dm^6 mol^{-2} s^{-1} and $K_1k_{DABCO} = 4·5$ dm^6 mol^{-2} s^{-1}

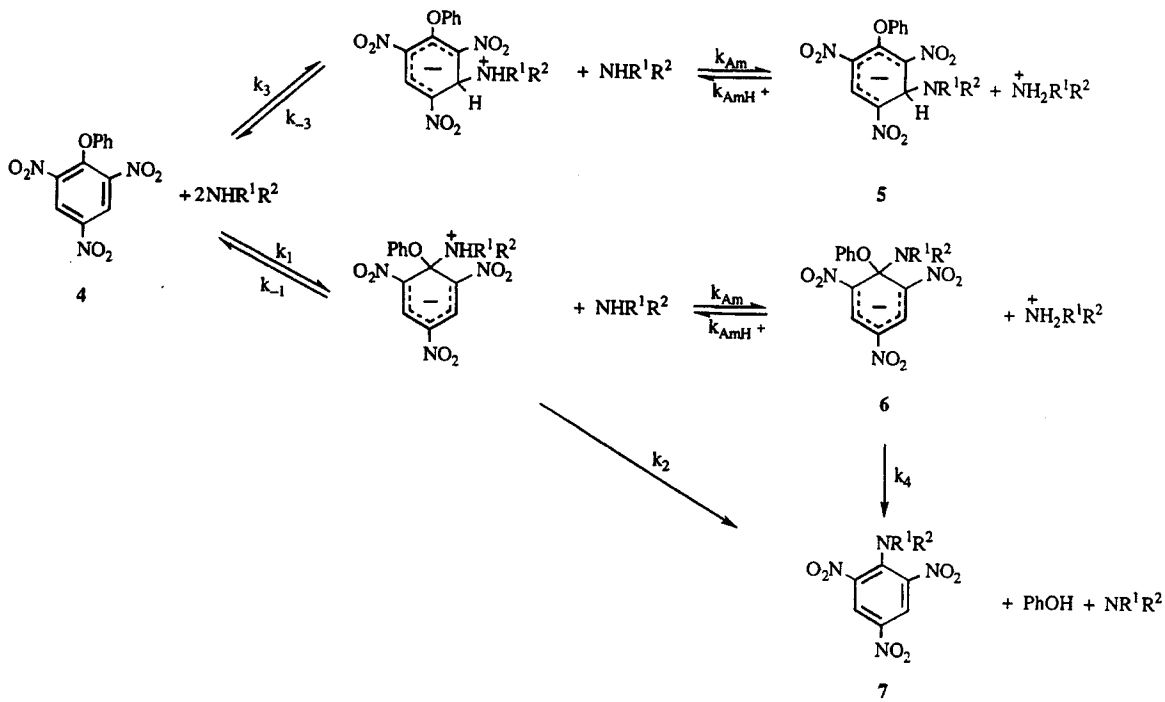
Phenyl 2,4-dinitrophenyl ether (9)

Reaction with morpholine occurred in a single kinetic process, giving 1-morpholino-2,4-dinitrobenzene with

Table 2. Kinetic data for reaction of **4** with morpholine in DMSO at 25 °C

[Morpholine]/ mol dm^{-3}	[Morpholinium perchlorate]/mol dm^{-3}	k^{a}_{obs}/s^{-1}	k^{b}_{calc}/s^{-1}	k^{c}_{obs}/10^{-3}s^{-1}	k^{d}_{calc}/10^{-3}s^{-1}
0·02	—	1·07	0·98	—	—
0·03	—	2·24	2·21	—	—
0·04	—	3·86	3·92	—	—
0·05	—	6·01	6·12	—	—
0·004	0·01	—	—	1·4	1·1
0·006	0·01	—	—	2·7	2·5
0·008	0·01	—	—	5·0	4·5
0·01	0·01	6·0	6·2	7·0	6·7
0·015	0·01	—	—	13	14
0·02	0·01	6·7	7·0	21	24
0·03	0·01	8·0	8·2	—	
0·04	0·01	9·8	9·9	—	
0·05	0·01	12·7	12·1	—	
0·10	0·01	29	30	—	

[a] Fast reaction, measured at 435 nm.
[b] Calculated from equation (3) with $K_3k_{Am} = 2450$ dm^{6}mol^{-2}s^{-1} and $k_{AmH^+} = 600$ dm^{3}mol^{-1}s^{-1}.
[c] Slow reaction, measured at 370 nm.



Scheme 3

Table 3. Kinetic data fo reaction of **8** with morpholine in DMSO at 25 °C

[Morpholine]/mol dm^{-3}	[DABCO]/mol dm^{-3}	$k^{a}_{obs}/10^{-3}$s^{-1}	$k^{b}_{calc}/10^{-3}$s^{-1}
0·01	—	1·2	1·1
0·02	—	4·4	4·4
0·03	—	9·9	9·9
0·04	—	17	18
0·05	—	26	27
0·02	0·05	8·6	8·9
0·02	0·10	13	13
0·02	0·15	18	18
0·02	0·20	23	23

[a] Measured at 410 nm, with **8** at 5×10^{-5} mol dm^{-3}.

λ_{max} 386 nm. A plot, not shown, of k_{obs} versus amine concentration was linear with a positive intercept, indicating that, in contrast with **4** and **8**, the uncatalysed step, k_2, makes a significant contribution to the reaction flux. The reaction is catalysed by DABCO, so that the rate expression

$$k_{obs} = K_1[Am](k_2 + k_{Am}[Am] + k_{DABCO}[DABCO]) \quad (9)$$

applies. Values calculated with $K_1k_2 = 3 \times 10^{-4}$ dm^{3}mol^{-1}s^{-1}, $K_1k_{Am} = 1{\cdot}3 \times 10^{-2}$ dm^{6}mol^{-2}s^{-1} and $K_1k_{DABCO} = 8 \times 10^{-3}$ dm^{6}mol^{-2}s^{-1} gave good agreement with experimental data (Table 4).

Our results with this compound are in general accord with those reported previously[8] for the reaction at 30·5 °C.

1-Chloro-2,4-dinitrobenzene (10)

The reactions of **10** with piperidine and with morpholine resulted in the formation of the corresponding 1-amino derivatives, λ_{max} 385 nm. Kinetic measurements with piperidine (0·01–0·10 mol dm^{-3}) and morpholine (0·05–0·125 mol dm^{-3}) showed a precise first-order dependence on the amine concentration. This indicates, in terms of Scheme 2, that nucleophilic attack by amine is rate limiting. The results yielded values for k_1 of 1·9 dm^{3}mol^{-1}s^{-1} with piperidine and 0·33 dm^{3}mol^{-1}s^{-1} with morpholine.

Reaction at unsubstituted ring positions

The data in Table 5 show that for formation of the adducts **3** the overall equilibrium constant, $K_{c,3}$ is 63 times smaller for morpholine than for piperidine. For attack at an unsubstituted ring-proton of **4** the ratio is 98. Values of K_3k_{Am} similarly have a large ratio for the two amines of *ca* 70. However, the values of k_{AmH+} are very similar. It has been argued previously[5,21] that in trinitro-activated substrates the ratio k_{Am}/k_{AmH+} will have a value of *ca* 500, reflecting the higher acidity of zwitterionic adducts, **2**, than of the corresponding ammonium ions. This ratio is not expected[5,21] to vary greatly with the nature of the substrate or of the amine; the morpholinium ion will be expected to be more acidic than the piperidinium ion, but similarly the zwitterion, **2**, from morpholine will be more acidic than that from

Table 4. Kinetic data for reaction of **9** with morpholine in DMSO at 25 °C

[Morpholine]/mol dm^{-3}	[DABCO]/mol dm^{-3}	$k^{a}_{obs}/10^{-3}$s^{-1}	$k^{b}_{calc}/10^{-3}$s^{-1}
0·05	—	0·43	0·47
0·075	—	1·03	0·96
0·10	—	1·7	1·6
0·15	—	3·7	3·4
0·20	—	6·0	5·8
0·25	—	8·8	8·9
0·10	0·05	2·1	2·0
0·10	0·10	2·5	2·4
0·10	0·15	2·8	2·8
0·10	0·20	3·4	3·2
0·10	0·25	3·7	3·6

[a] Measured at 385 nm with **9** at 5×10^{-5} mol dm^{-3}.
[b] Calculated from equation (9) with $K_1k_2 = 3 \times 10^{-4}$ dm^{3}mol^{-1}s^{-1}, $K_1k_{Am} = 1{\cdot}3 \times 10^{-2}$ dm^{6}mol^{-2}s^{-1} and $K_1k_{DABCO} = 8 \times 10^{-3}$ dm^{6}mol^{-2}s^{-1}

Table 5. Summary and comparison of data for morpholine and piperidine[a]

Compound	Parameter	Piperidine[b]	Morpholine	Piperidine/morpholine
Reaction at unsubstituted positions				
1	$K_{c,3}$/dm^3 mol^{-1}	2140	34	63
	K_3k_{Am}/dm^6 mol^{-2} s^{-1}	6×10^5	8500	71
	k_{AmH^+}/dm^3 mol^{-1} s^{-1}	280	250	1·1
4	$K_{c,3}$/dm^3 mol^{-1}	400	4·1	98
	K_3k_{Am}/dm^6 mol^{-2} s^{-1}	$1·7\times10^5$	2450	69
	k_{AmH^+}/dm^3 mol^{-1} s^{-1}	400	600	0·7
Reaction at substituted positions				
4	K_1k_{Am}/dm^6 mol^{-2} s^{-1}	3000	70	43
8	K_1k_{Am}/dm^6 mol^{-2} s^{-1}	550	11	50
	k_{Am}/k_{DABCO}	6·5	2·4	—
9	K_1k_{Am}/dm^6 mol^{-2} s^{-1}	0·8	0·013	62
	K_1k_2/dm^3 mol^{-1} s^{-1}	0·005	3×10^{-4}	17
	k_{Am}/k_{DABCO}	6·2	1·6	—
10	k_1/dm^3 mol^{-1} s^{-1}	1·9	0·33	6

[a] Salt concentration 0·01 mol dm^{-3} except for **1** (0·1 mol dm^{-3}). Data have not been statistically corrected.
[b] Data from Refs 6 and 14.

piperidine. Since values of k_{AmH^+} are similar for the two amines, values of k_{Am} will also be similar. That these values, reflecting proton transfer between nitrogen atoms, are much lower than the diffusion limit probably indicates steric hindrance to approach of the reagents. It follows that the difference by a factor of *ca* 70 in the values of $K_{c,3}$ and of K_3k_{Am} is due to a difference in the values of K_3, the higher value for piperidine reflecting its higher basicity.

Comparison of data for **1** and **4** shows that for each amine values of $K_{c,3}$ and K_3k_{Am} are *ca* five times lower for the 1-phenoxy derivative. The σ_{meta} value for the phenoxy group[22] is 0·25 so that it should have a favourable electronic effect on amine addition at the 3-position. However, the results show that this is more than balanced by an unfavourable steric effect. Thus the nitro-groups at the 2- and 6-positions will be rotated from the ring plane so that they cannot exert their maximum electron-withdrawing influence. For **1** and **4** the steric situation at the reaction centre, the unsubstituted 3-position, should be similar, leading to similar values of k_{Am} and of k_{AmH^+} for the two compounds.

Reaction at Substituted Positions

Our results indicate that for each phenyl ether the substitution reaction shows a squared dependence on the amine concentration and is catalysed by DABCO. This indicates that the rate-determining step is proton transfer. We have argued previously[13,14] that, with reference to Scheme 3, this proton transfer is likely to be from the zwitterionic intermediate to amine, the k_{Am} step, rather than from the ammonium ion to the anionic adduct, the k_4 step. Briefly, our arguments were based on the failure to observe intermediates, such as **6**, on the reaction pathway and on pyrrolidine to piperidine reactivity ratios. The results in Table 5 are readily explained on the basis that the rate-limiting proton transfer is from zwitterion to amine. Thus values of K_1k_{Am} are, for **4**, **8** and **9**, *ca* 50 times lower for morpholine than for piperidine. As for reaction at unsubstituted positions, this value reflects lower values of K_1 for morpholine than for piperidine, whereas values of k_{Am} for the two amines are expected to be similar.

The observation of base catalysis in nucleophilic substitution reactions depends on the value of the ratio k_{Am}/k_{-1}. A lower value of this ratio, leading to the condition $k_{-1} \gg k_{Am}[Am]$, results in the reaction showing susceptibility to base catalysis. We were not able to measure directly k_{Am}/k_{-1} ratios. However, our results show that values of k_{Am} are expected to be similar for reactions of morpholine and piperidine whereas values of K_1 will be lower for morpholine. Lower values of K_1 are likely to be due to lower values of k_1 and higher values of k_{-1}. For comparison, the value of k_1 for reaction of morpholine with **10** is six times lower than that for reaction of piperidine. A similar ratio for k_1

values in reactions with the phenyl ethers would lead to values of k_{-1} *ca* ten times larger for the morpholine than for the piperidine reactions. Hence it is expected that the k_{Am}/k_{-1} values will be lower for reactions with morpholine than for corresponding reactions with piperidine. This explains the observations[18,19] that reactions involving morpholine are in general more susceptible to base catalysis than those involving piperidine.

The values of k_{Am}/k_{DABCO} are slightly higher for reactions involving piperidine than for those with morpholine. This ratio reflects the ability of the amine relative to DABCO to extract a proton from the zwitterionic intermediate. Given the considerably higher basicity of piperidine than of morpholine, the general similarity in the observed k_{Am}/k_{DABCO} ratios is additional evidence that steric considerations are of major importance in determining the rate of the proton transfer.

Only in the case of the least activated substrate, **9**, were we able to observe uncatalysed conversion of the zwitterion to products, the k_2 step. It is interesting that the K_1k_2 ratio is reduced to 17 for reaction of piperidine versus morpholine. Since the K_1 ratio is likely to be at least 50, this implies that the value of k_2 is higher for the morpholine than for the piperidine reaction. This is compatible with the k_2 step involving direct intramolecular proton transfer within the zwitterion, since the morpholinium group should be more acidic than its piperidinium counterpart.

REFERENCES

1. F. Terrier, *Nucleophilic Aromatic Displacement*. VCH, New York (1991).
2. J. F. Bunnett and R. E. Zahler, *Chem. Rev.* **49**, 275 (1991).
3. C. F. Bernasconi, *MTP International reviews of science. Organic chemistry series one*, Vol. 3, p.33. Butterworth, London (1973).
4. J. Hirst, *J. Phys. Org. Chem.* **7**, 68 (1994).
5. M. R. Crampton and B. Gibson, *J. Chem. Soc., Perkin Trans.* 2 533 (1981).
6. M. R. Crampton and C. Greenhalgh, *J. Chem. Soc., Perkin Trans.* 2 1175 (1983).
7. C. F. Bernasconi, M. C. Muller and P. Schmid, *J. Org. Chem.*, **44**, 3189 (1979).
8. D. Ayediran, T. O. Bamkole, J. Hirst and I. Onyido, *J. Chem. Soc., Perkin Trans.* 2 597, 1580 (1977).
9. J. Hirst, G. Hussain and I. Onyido, *J. Chem. Soc., Perkin Trans.* 2 397 (1986).
10. T. A. Emokpae, P. U. Uwakwe and J. Hirst, *J. Chem. Soc., Perkin Trans.* 2 125 (1993).
11. J. A. Orvik and J. F. Bunnett, *J. Am. Chem. Soc.*, **92**, 2417 (1970).
12. M. R. Crampton and P. Routledge, *J. Chem. Soc., Perkin Trans.* 2 573 (1984).
13. R. Chamberlin and M. R. Crampton, *J. Chem. Soc., Perkin Trans.* 2 425 (1994).
14. R. Chamberlin and M. R. Crampton, *J. Chem. Soc., Perkin Trans.* 2 1831 (1995).
15. S. Sekiguchi, M. Hosokawa, T. Suzuki and M. Sato, *J. Chem. Soc., Perkin Trans.* 2 1111 (1993).
16. C. F. Bernasconi and P. Schmid, *J. Org. Chem.* **32**, 2953 (1967).
17. J. F. Coetzee, *Prog. Phys. Org. Chem.* **4**, 45 (1967).
18. R. E. Akpojivi, T. A. Emokpae and J. Hirst, *J. Chem. Soc., Perkin Trans.* 2 443 (1994).
19. D. Ayediran, T. O. Bamkole and J. Hirst, *J. Chem. Soc., Perkin Trans.* 2 1396 (1976).
20. R. Chamberlin and M.R. Crampton, *J. Chem. Res.* (*S*) 106; (*M*) 811 (1993).
21. C. F. Bernasconi, M. C. Muller and P. Schmid, *J. Org. Chem.* **44**, 3189 (1979).
22. D. H. McDaniel and H. C. Brown, *J. Org. Chem.* **23**, 420 (1958).