JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
*J. Phys. Org. Chem.* 2005; **18:** 844–849
Published online 20 May 2005 in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/poc.949

# Kinetics of base-catalysed ring closure of methyl 2,6-dinitrophenylsulfanylethanoate†

**Marek Janík, Vojeslav Štěrba, Jiří Černý, Vladimír Macháček* and Petr Jansa**

Faculty of Chemical Technology, Department of Organic Chemistry, University of Pardubice, Nám. Čs. Legií 565, CZ-53210 Pardubice, Czech Republic

*Received 14 February 2005; accepted 21 March 2005*

ABSTRACT: The base-catalysed ring closure of methyl 2,6-dinitrophenylsulfanylethanoate gives 2-methoxycarbonyl-7-nitrobenzo[*d*]thiazole-3-oxide. The kinetics of this ring closure were studied by means of UV–visible spectrophotometry in methanolic buffers of *N*-methylmorpholine–*N*-methylmorpholinium chloride and *N*-methylpiperidine–*N*-methylpiperidinium chloride at 25 °C at ionic strength $I = 0.1\ \mathrm{mol\,l^{-1}}$. The dependences of $k_{obs}$ on the base concentration are not linear, their slopes decreasing with increasing base concentration at constant ratio of the buffer components. The reaction mechanism was suggested on the basis of comparison with the ring closure kinetics of methyl 2,4,6-trinitrophenylsulfanylethanoate. The rate-limiting step of the reaction sequence consists in formation of the conjugated base of substrate **1**. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: ring closure reaction; base catalysis; reaction kinetics; heterocyclic nitrones

## INTRODUCTION

Our previous paper dealt with the kinetics of ring closure of methyl 2,4,6-trinitrophenylsulfanylethanoate[1] in acetate, methoxyacetate and *N*-methylmorpholine buffers in methanol. In the acetate and methoxyacetate buffers, the dependences of the observed rate constant $k_{obs}$ on the concentration of base were linear in the whole concentration range studied, but the slopes of these dependences increased with increase in the basicity of the medium, which means that the ring closure went by two reaction pathways, out of which one had its reaction rate dependent on the concentration of carboxylate only and the other on the concentration of carboxylate and methoxide. Hence the reaction was subject to general base catalysis with the value of the Brønsted coefficient $\beta = \Delta\log k / \Delta\mathrm{p}K_a \approx 0.8$.[1]

The ring closure of methyl 2,4,6-trinitrophenylsulfanylethanoate in *N*-methylmorpholine buffer also exhibited general base catalysis, but the slopes of the dependences of $k_{obs}$ on the concentration of base decreased with increasing concentration of base, and this decrease was the faster the more acidic was the medium (i.e. the lower the ratio of buffer components [B]/[$BH^+$]).

**Correspondence to:* V. Macháček, Faculty of Chemical Technology, Department of Organic Chemistry, University of Pardubice, Nám. Čs. Legií 565, CZ-53210 Pardubice, Czech Republic.
E-mail: vladimir.machacek@upce.cz
*Contract/grant sponsor:* Ministry of Education, Youth and Sports of the Czech Republic; *Contract/grant number:* CIMSM 0021627501.
*Contract/grant sponsor:* Czech Science Foundation; *Contract/grant number:* 203/01/0227.
†Selected paper presented for a special issue dedicated to Professor Otto Exner on the occasion of his 80th birthday.

The rate constant $k_{obs}$ of the ring closure in methoxyacetate buffers corrected by means of the $\beta$ value to the $\mathrm{p}K_a$ corresponding to *N*-methylmorpholinium was about 40 times lower than the experimentally measured rate constant of the reaction catalysed by *N*-methylmorpholine. In the Brønsted relationships given in the literature, these constants do not differ or differ only slightly.

For these reasons, we decided to study the kinetics of ring closure using different tertiary amines as catalysts. Since the application of *N*-methylmorpholine makes the ring closure extraordinarily sterically demanding, we chose as different base *N*-methylpiperidine, whose steric requirements are similar to those of the previously used *N*-methylmorpholine. However, the ring closure of methyl 2,4,6-trinitrophenylsulfanylethanoate catalysed with *N*-methylpiperidine was so fast that it was impossible to obtain reliable values of the rate constants, which is why we used methyl 2,6-dinitrophenylsulfanylethanoate, which undergoes a slower ring closure.

## EXPERIMENTAL

### Compounds

2,6-Dinitrochlorobenzene was prepared according to Ref. 2 or analogously from 2,6-dinitrophenol according to Ref. 3.

To prepare methyl 2,6-dinitrophenylsulfanylethanoate (**1**) and 2-methoxycarbonyl-7-nitrobenzo[*d*]thiazole-3-oxide (**2**), a solution of 4.05 g (20 mmol) of 2,6-dinitrochlorobenzene in 25 ml of 1,2-dimethoxyethane was stirred by means of a magnetic stirrer under an argon

atmosphere and treated with a solution of 2.12 g (20 mmol) of methyl sulfanylethanoate in 15 ml of 1,2-dimethoxyethane added at once. Thereafter, a solution of 2.78 ml (20 mmol) of triethylamine in 10 ml of 1,2-dimethoxyethane was added drop by drop within 3.5 h. The mixture was stirred at room temperature for a further 1 h, then poured in 100 ml of dilute HCl (ca 5%), and the separated solid was collected by filtration. The yellow–red product obtained (4.22 g) was separated by column chromatography [silica gel; $CHCl_3$–ethyl acetate (9:1, v/v)].

Methyl 2,6-dinitrophenylsulfanylethanoate (**1**) ($R_F \approx 0.5$) was recrystallized from methanol; yield 2.16 g (40%) of light yellow compound (**1**), m.p. 88.5–90.5 °C. $^1$H NMR ($CDCl_3$), $\delta$ 7.92 ($A_2$ part) and 7.72 (B part) of $A_2B$ system, 3H, $^3J = 8.1$ Hz (Ar); 3.72 s, 2H, ($CH_2$); 3.69 s, 3H, ($CH_3$). $^{13}$C NMR ($CDCl_3$): $\delta$ 168.3 (CO); 155.6 (C-2,6); 131.3 (C-4); 126.6 (C-3,5); 120.9 (C-1); 52.7 ($CH_3$); 38.2 ($CH_2$). For $C_9H_8N_2O_6S$ (272.24): calculated C 39.71, H 2.96, N 10.29, S 11.78; found C 39.46, H 3.01, N 10.47, S 11.49%.

2-Methoxycarbonyl-7-nitrobenzo[*d*]thiazole-3-oxide (**2**) ($R_F \approx 0.25$) was recrystallized from methanol; yield 0.36 g (7.1%), b.p. 200–201 °C (ref.[4] 202–203 °C). $^1$H NMR (DMSO-$d_6$): $\delta$ 8.82 dd, 1H, (H-6, $^3J = 8.1$ Hz, $^4J = 0.8$ Hz); 8.63 dd, 1H, (H-4, $^3J = 8.1$ Hz, $^4J = 0.8$ Hz); 8.03 t, 1H, (H-5, $^3J = 8.1$ Hz). $^{13}$C NMR (DMSO-$d_6$): $\delta$ 157.1 (CO); 146.1, 142.2, 134.9, 123.2 ($4 \times C_q$); 128.9, 127.3, 125.2 ($3 \times$ CH); 53.1 ($CH_3$). For $C_9H_6N_2O_5S$ (254.22): calculated C 42.52, H 2.38, N 11.02, S 12.61; found C 42.76, H 2.58, N 11.09, S 12.82%.

The NMR spectra were measured using a Bruker Avance 500 spectrometer (500.13 MHz for $^1$H and 125.77 MHz for $^{13}$C). Hexamethyldisiloxane was used as the internal standard for $^1$H NMR ($\delta$ 0.05). The $^{13}$C NMR spectra were standardized by means of the middle signal of the solvent multiplet ($\delta$ 77.0 in $CDCl_3$ and 39.6 in DMSO-$d_6$).

### $\Delta pK_a$ values of buffers

The $\Delta pK_a$ values between acetic acid, *N*-methylmorpholinium and *N*-methylpiperidinium were determined spectrophotometrically from the absorptions of indicators (2-chloro-4-nitrophenol and 4-nitrophenol) using the procedure described previously.[1] Using the $pK_a$ value of acetic acid in methanol of 9.52,[5] we found $pK_a$ values of 9.12 and 11.05 for *N*-methylmorpholinium and *N*-methylpiperidinium, respectively.

### Kinetic measurements

The quality of methanol was checked by means of UV–visible spectrophotometry. The absorbance of the pure solvent against an empty cell was <0.08 in the wavelength range above 250 nm.

Anhydrous sodium perchlorate (p.a.) for adjustment of ionic strength was dried at 100 °C/2.6 kPa for 6 h. *N*-Methylpiperidine (Aldrich, 99%) was distilled, and the fraction with b.p. 106–107 °C was used. *N*-Methylmorpholine (Aldrich, 99.5+%) was distilled, and the fraction with b.p. 115–116 °C was used.

### Preparation of buffers

The buffers were prepared from methanolic 1 mol l$^{-1}$ solutions of *N*-methylpiperidine, *N*-methylpiperidium chloride, *N*-methylmorpholine and *N*-methylmorpholinium chloride. The solutions of ammonium chlorides were prepared *in situ* by neutralizing the solutions of the respective amines with a fresh methanolic solution of hydrochloric acid of known concentration with intense cooling. The stock solutions were used to prepare the buffers with ionic strength $I = 0.1$ mol l$^{-1}$ determined by the ionic component of the buffer, and with the component ratios [base]/[acid] = 8:1, 6:1, 4:1, 2:1 and 1:1.

Further, from the buffers thus obtained we prepared buffers of given ratios of components, but with varying concentrations; their ionic strength was adjusted to $I = 0.1$ mol l$^{-1}$ by addition of sodium perchlorate solution (1 mol l$^{-1}$). For the kinetic measurements, compounds **1** and **2** were dissolved in suitable solvents ($CHCl_3$, acetone); these solutions were prepared immediately before the measurement proper.

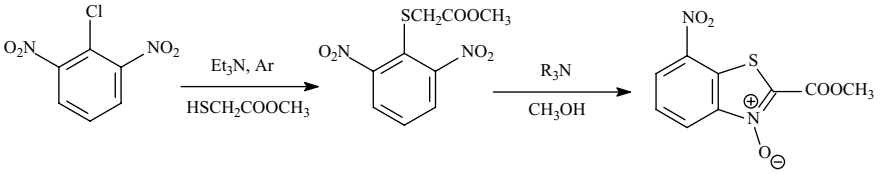
### Kinetic experiments

All the kinetic measurements were carried out with a Hewlett-Packard Model 8453A diode-array Spectrophotometer at 25 ± 0.1 °C at a wavelength of 375 nm with substrate concentrations of ca $5 \times 10^{-3}$ mol l$^{-1}$. In preliminary experiments, the absorbance changes were scanned in the wavelength range 250–400 nm.

## RESULTS AND DISCUSSION

The ring closure of compound **1** (Scheme 1) was studied spectrophotometrically at 25 °C under conditions of pseudo-first order in methanolic buffers. Under the conditions of the kinetic experiments, the cyclization product is formed almost quantitatively (>96%). The half-lives of ring closure reactions of compound **1** to compound **2** were in the range from ca 75 s to 10 000 s, depending on the composition of the buffer.

All the values of observed rate constants $k_{obs}$ in methanolic buffers are given in Tables 1 and 2. The dependences of $k_{obs}$ on the base concentration are not




**Scheme 1**

**Table 1.** Values of observed rate constants $k_{obs}$ ($s^{-1}$) of ring closure **1** → **2** in methanolic buffers of *N*-methylmorpholine–*N*-methylmorpholinium chloride at 25 °C and $I = 0.1$ mol $l^{-1}$

| [B]/[BH] | [B] | $k_{obs} \times 10^4$ | [B]/[BH] | [B] | $k_{obs} \times 10^4$ |
|---|---|---|---|---|---|
| 6:1 | 0.60 | 1.689 | 4:1 | 0.40 | 1.206 |
| | 0.54 | 1.684 | | 0.30 | 1.166 |
| | 0.48 | 1.659 | | 0.20 | 1.106 |
| | 0.42 | 1.657 | | 0.10 | 0.948 |
| | 0.36 | 1.621 | | 0.06 | 0.855 |
| | 0.30 | 1.580 | | 0.04 | 0.791 |
| | 0.24 | 1.513 | | 0.02 | 0.707 |
| | 0.18 | 1.472 | | | |
| | 0.12 | 1.336 | | | |
| | 0.06 | 1.163 | | | |

**Table 2.** Values of observed rate constants $k_{obs}$ ($s^{-1}$) of ring closure **1** → **2** in methanolic buffers of *N*-methylpiperidine–*N*-methylpiperidinium chloride at 25 °C and $I = 0.1$ mol $l^{-1}$

| [B]/[BH] | [B] | $k_{obs} \times 10^3$ | [B]/[BH] | [B] | $k_{obs} \times 10^3$ |
|---|---|---|---|---|---|
| 1:1 | 0.10 | 2.61 | 2:1 | 0.05 | 4.53 |
| | 0.075 | 2.59 | | 0.03 | 4.20 |
| | 0.05 | 2.54 | | 0.01 | 3.54 |
| | 0.025 | 2.29 | 4:1 | 0.40 | 8.95 |
| | 0.01 | 1.99 | | 0.30 | 9.00 |
| 2:1 | 0.20 | 5.00 | | 0.20 | 8.93 |
| | 0.18 | 4.96 | | 0.10 | 8.64 |
| | 0.15 | 4.98 | | 0.06 | 8.15 |
| | 0.13 | 4.97 | | 0.04 | 7.54 |
| | 0.10 | 4.88 | | 0.02 | 6.95 |
| | 0.08 | 4.77 | | | |

linear, their slopes decreasing with increasing base concentration at a constant ratio of the buffer components (as in the case of ring closure of methyl 2,4,6-trinitrophenylsulfanylethanoate). The dependences of $k_{obs}$ vs concentration of base and ratio of buffer components are shown in Figs 1 and 2.

The dependences of $k_{obs}$ on concentration of base and on ratio of the buffer components indicate that (i) the reaction is subject to general base catalysis; (ii) increasing concentration of buffer causes an increasing manifestation of the reverse reaction of some of the intermediates (the cyclization product, compound **2**, is stable in the reaction medium and does not undergo the reverse reaction); (iii) the reverse reaction is the faster the more acidic the buffer used is.

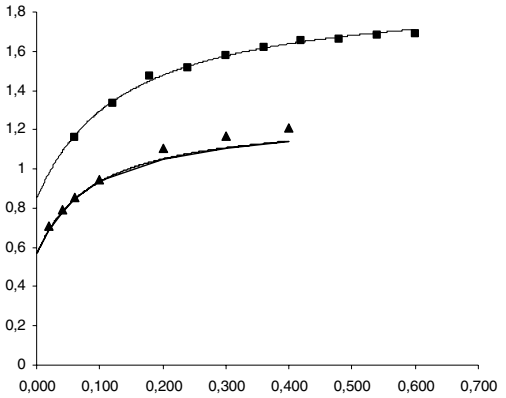



**Figure 1.** Dependence of observed rate constants $k_{obs} \times 10^4$ ($s^{-1}$) of ring closure of methyl 2,6-dinitrophenylsulfanylethanoate (ordinate) on concentration of *N*-methylmorpholine (mol $l^{-1}$) (absassa) in buffers with component ratios [B]/[$BH^+$] = 6:1 (■) and 4:1 (▲)

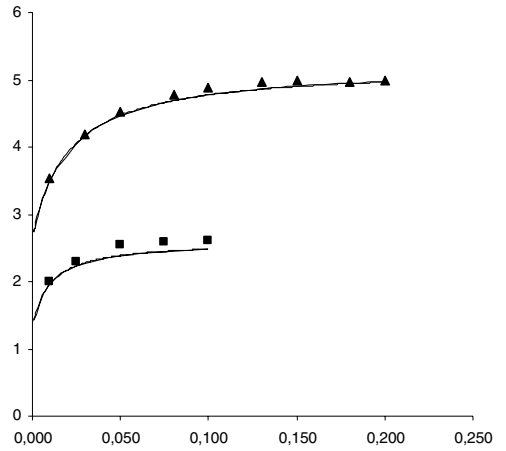
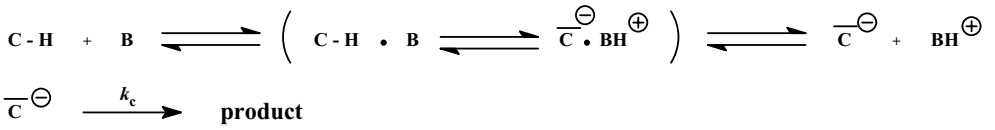



**Figure 2.** Dependence of observed rate constants $k_{obs} \times 10^3$ ($s^{-1}$) of ring closure of methyl 2,6-dinitrophenylsulfanylethanoate (ordinate) on concentration of *N*-methylpiperidine (mol $l^{-1}$) (absassa) in buffers with component ratios [B]/[$BH^+$] = 1:1 (■) and 2:1 (▲)

Therefrom it follows that the rate of the reverse reaction depends on the concentration of the acidic buffer component, [$BH^+$]. A simplified representation of the ring closure reaction is given in Scheme 2, where C—H is the substrate **1**, and $C^-$ stands for the conjugated base of substrate.



**Scheme 2**

The kinetic equation of the ring closure reaction catalysed by the basic component of buffer and by methoxide ion is

$$k_{obs} = \frac{(k_B[B] + k_{MeO^-}[MeO^-])k_c}{k_{BH^+}[BH^+] + k_c} = \frac{k_B[B] + k_{MeO^-}[MeO^-]}{\frac{k_{BH^+}}{k_c}[BH^+] + 1} \quad (1)$$

where $k_B$ and $k_{MeO^-}$ are the rate constants of the reactions catalysed by the basic component of buffer and by methoxide, respectively; $k_{BH^+}$ is the rate constant of the reverse reactions catalysed by ammonium ion. The calculated values of $k_B$ and $k_{BH^+}/k_c$ are $(1.40 \pm 0.4) \times 10^{-3}\,l\,mol^{-1}\,s^{-1}$ and $44 \pm 11$ for the *N*-methylmorpholine buffer and $(260 \pm 60) \times 10^{-3}\,l\,mol^{-1}\,s^{-1}$ and $100 \pm 25$ for the *N*-methylpiperidine buffer. The constant $k_{MeO^-}$ has a value of $930 \pm 80\,l\,mol^{-1}\,s^{-1}$.

The primarily formed carbanion (conjugated base of substrate **1**) is gradually transformed into the product via a sequence of several reactions (Scheme 3).

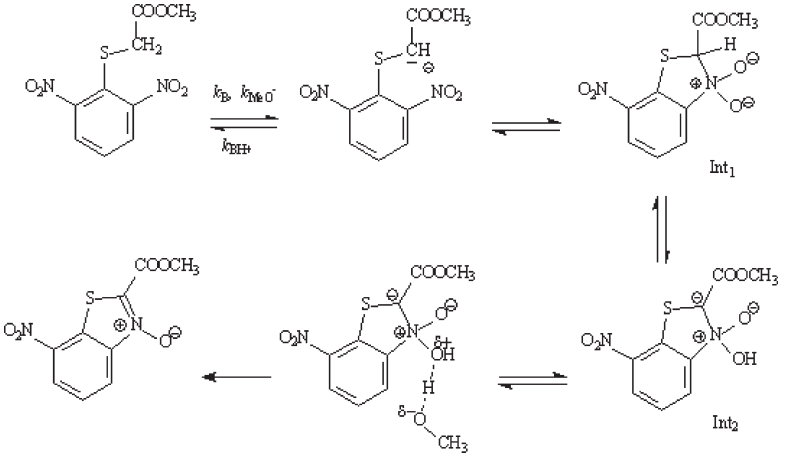
Potential acid catalysis by the action of $BH^+$ in the removal of water from $Int_2$ (giving the cyclization product) could not slow the ring closure with increasing concentration of $BH^+$. The transformation of $Int_1$ into $Int_2$ is catalysed by base: the fast removal of the proton from the C—H group of $Int_1$ with concomitant formation of ammonium ion $BH^+$ is greatly facilitated by the bond of this group to the positively charged nitrogen (CH—$N^+$). Then there follows a fast protonation of the negatively charged oxygen by the $BH^+$ ion; the second possibility is a concerted proton transfer from carbon to oxygen by action of methanol (proton switch).

Since the ring closure reaction is subject to general base catalysis, its rate depends on the rate of transformation of the encounter complex C—H·B into $C^-$ and $BH^+$ (Scheme 2). The effect of changing structure of the base on the change in this velocity is given by the Brønsted coefficient $\beta$ according to the relation $\beta = d(\log k_B)/d(pK_a)$, and in the case of this thermodynamically very unfavourable reaction it has a value of $\sim 1.2$ ($\alpha \approx -0.2$) (Amyes and Richard[6] found a value of $\beta = 1.09$ for deprotonation of ethyl acetate by 3-substituted quinuclidines in aqueous solution). The value of $\beta = 1$ for a reaction subject to general base catalysis as represented in Scheme 2 means that the rate-limiting step is diffusion separation of the complex[7] $C^-\cdot BH^+$ into $C^-$ and $BH^+$. The Brønsted plot of CH acids with approximately $0.8 < \beta < 1$ corresponds to an Eigen-type mechanism of proton transfer in which both proton transfer and diffusional separation of the $C^-\cdot BH^+$ complex are partially rate determining. In reality, however, both the starting base and the conjugated acid formed are solvated, but the removal of proton from the CH-acid by amines and oxygen bases and the reverse step occur directly and are not mediated by an intervening water (or other protic solvent).[8–10]

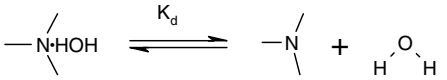
Because the reference equilibrium reaction is the ionization of solvated acid to solvated conjugated base, a correction to $\beta_{obs}$ must be made [Eqns (2)–(5)[11]]:

$$\beta_d = \frac{d(\log K_d)}{d(\log K_a)} = -0.2 \quad (2)$$

$$\beta_{corr} = \frac{\beta_{obs} - \beta_d}{1 - \beta_d} \quad (3)$$



**Scheme 3**



**Scheme 4**

$$\beta_s = \frac{d(\log K_s)}{d(\log K_a)} \quad (4)$$

$$\beta_{corr} = \frac{\beta_{obs}}{1+\beta_s} \quad (5)$$

where $K_s$ and $K_d$ are equilibrium constants of solvation and desolvation, respectively, of the ionic component of the acid–base pair and $K_a$ is the dissociation constant of the conjugated acid.[12] In the case of the starting amine, this means a correction for the effect of structure of the amine on its desolvation (Scheme 4).

The magnitude of correction $\beta_{corr}$ decreases with increasing value of $\beta_{obs}$, being zero for $\beta_{obs} = 1$. In the case of the conjugated acid of the amine, this means a correction for the effect of changing structure on the solvation; the $\beta_s$ value suggested for substituted carboxylic acids and alcohols is +0.2;[12,13] no $\beta_s$ value was found in the literature for tertiary amines. Protonated tertiary amines in water are much more strongly solvated than carboxylic acids or alcohols, but in methanol the solvation is substantially weaker and, hence, changes in solvation with changes in structure will also be smaller; if we adopt the same value of $\beta_s$ as that used for carboxylic acids, then $\beta_{corr}$ for the ring closure of methyl 2,6-dinitrophenylsulfanylethanoate catalysed by tertiary amines will be $\beta_{corr} \approx 1.20/1.20 \approx 1$; this means that the rate-determining step is the diffusional separation of ion pair $BH^+ \cdot C^-$, the reverse reaction being an encounter-limited reaction[14] ($k \approx 5 \times 10^9\,l\,mol^{-1}\,s^{-1}$) of $C^-$ with desolvated $BH^+$. The free carbanion can react further, eventually giving the final product, or can give the starting C-acid **1** by the reverse reaction with desolvated $BH^+$.

A similar correction of the Brønsted coefficient $\beta_{obs} = 0.80$ in the reactions of methyl 2,4,6-trinitrophenylsulfanylethanoate in buffers composed of carboxylic acids and carboxylates with an estimated $\beta_s$ in methanol of +0.15 will give the value $\beta_{corr} = 0.7$, i.e. the rate-limiting step is the proton transfer $RCOO^- \cdot CH \rightarrow RCOOH \cdot C^-$, because the reverse protonation of the carbanion is much slower than the diffusional separation of the complex $RCOOH \cdot C^-$; the rate-limiting step of the reverse reaction is protonation of carbanion by carboxylic acid. This reaction in carboxylate buffers is ca 40 times faster than the analogous reaction in amine buffers. The reverse protonation of carbanion by carboxylic acid is much slower than the consecutive ring closure, so it does not make itself felt even at higher concentrations of buffer—the dependences of $k_{obs}$ vs buffer concentration are (with the ratio of buffer components kept constant) linear over the whole interval measured. The much slower reaction of the 2,4,6-trinitro derivative with methoxyacetate ion than that with *N*-methylmorpholine probably occurs because the p$K_a$ values of carboxylic acids and tertiary amines were determined in a different medium from that in which the proton transfers from trinitro derivative to acetate or amine take place (in the sense that the p$K_a$ values are measured with the substances in the solvated state whereas the proton transfers proceed with the ions partially desolvated).

Methyl 2,6-dinitrophenylsulfanylethanoate (**1**) reacts several orders of magnitude faster than its isomer, the 2,4-dinitro derivative, which does not undergo ring closure at all.[1] The reason lies in the structure of methyl 2-nitro-6-substituted-phenylsulfanylethanoates, which was proved in some cases by means of X-ray analysis.[15] The nitro group at the 2-position is oriented almost perpendicularly to the benzene nucleus. This orientation makes it possible to bring together two reactants in a near attack conformation[16] (NAC), similar to that of some enzymes.

## CONCLUSIONS

The ring closure of methyl 2,6-dinitrophenylsulfanylethanoate (**1**) giving 2-methoxycarbonyl-7-nitrobenzo[*d*]thiazole-3-oxide (**2**) in methanolic buffers of *tert*-amine–*tert*-ammonium chloride is subject to general base catalysis. The dependences of the observed rate constant $k_{obs}$ on the concentration of buffers with constant ratios of the acidic to basic buffer components are not linear: at higher concentrations of buffers the slopes of the dependences decrease. The dependence deviates more from linearity the lower the ratio of concentrations of buffer components $[B]/[BH^+]$ is, i.e. the more acidic the buffer is. The dependences found are interpreted by the ring closure mechanism suggested. The rate-limiting step of the reaction consists in diffusion separation of the ion pair $C^- \cdot BH^+$ into free carbanion and protonated amine. The carbanion formed can react in a sequence of reaction steps, eventually giving the product, which is stable in the reaction medium, or it can react with the protonated amine to give the starting substrate. The rate of the reverse reaction increases with increasing concentration of the protonated amine, and at a sufficient concentration the rates of the reactions in both directions become equal, and $k_{obs}$ does not change any further with increasing buffer concentration. For the reactions in carboxylate buffers[1] at the buffer concentrations used, the rate-limiting step is proton transfer from C-acid to carboxylate ion, and the reverse reaction is not manifested kinetically.

### Acknowledgements

The authors are indebted to the Ministry of Education, Youth and Sports of the Czech Republic (Research Project CIMSM 0021627501) and the Czech Science Foundation (Grant No. 203/01/0227) for financial support.

## REFERENCES


1. Janík M, Macháček V, Pytela O. *Collect. Czech. Chem. Commun.* 1997; **62**: 1429–1445.
2. Gunstone FD, Horwood Tucker S. *Org. Synth., Coll. Vol.* **4**: 160–161.
3. Jefremow NN. *J. Russ. Phys. Chem. Ges.* 1918; **50**: 421–430.
4. Wagner K, Heitzer H, Oehlmann L. *Chem. Ber.* 1973; **106**: 640–654.
5. Moreau C. *Bull. Soc. Chim. Fr.* 1968; **1**: 31.
6. Amyes TL, Richard JP. *J. Am. Chem. Soc.* 1996; **118**: 3129–3141.
7. Eigen M. *Angew. Chem. Int. Ed. Engl.* 1964; **3**: 1–19.
8. Hibbert F. In *Comprehensive Chemical Kinetics*, Vol 8, Bamford CH, Tipper CFH (eds). Elsevier: Amsterdam, 1977; 97–196.
9. Bednar RA, Jencks WP. *J. Am. Chem. Soc.* 1985; **107**: 7117–7126.
10. Bednar RA, Jencks WP. *J. Am. Chem. Soc.* 1985; **107**: 7126–7134.
11. Jencks WP, Haber MT, Herschlag D, Nazaretian KL. *J. Am. Chem. Soc.* 1986; **108**: 479–483.
12. Murray CJ, Jencks WP. *J. Am. Chem. Soc.* 1988; **110**: 7561–7563.
13. Murray CJ, Jencks WP. *J. Am. Chem. Soc.* 1990; **112**: 1880–1889.
14. McClelland RA, Cozens FL, Steenken S, Amyes TL, Richard JP. *J. Chem. Soc., Perkin Trans. 2* 1993; 1717–1722.
15. Bertolasi V, Dudová K, Šimůnek P, Černý J, Macháček V. *J. Mol. Struct.* 2003; **658**: 33–42.
16. Bruice TC, Lightstone FC. *Acc. Chem. Res.* 1999; **32**: 127–136.