JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2006; **19:** 61–67
Published online 7 November 2005 in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/poc.999

Study of ring closure reaction of substituted phenyl *N*-(2-thiocarbamoylphenyl)carbamates catalysed by methoxide ion

Jiří Hanusek,* Miloš Sedlák, Petr Jansa and Vojeslav Štěrba

Department of Organic Chemistry, Faculty of Chemical Technology, University of Pardubice, Nám. Čs. legií 565, 532 10 Pardubice, Czech Republic

Received 4 July 2005; revised 22 September 2005; accepted 27 September 2005

ABSTRACT: Studies were made of the kinetics of methoxide ion-catalysed reactions of seven substituted phenyl *N*-(2-thiocarbamoylphenyl)carbamates, 4-methoxyphenyl *N*-(2-thiocarbamoylphenyl)-*N*-(methyl)carbamate and five substituted phenyl *N*-(4-thiocarbamoylphenyl)carbamates, leading to the respective cyclisation products (i.e. 4-thioxo-1*H*,3*H*-quinazolin-2-one or 1-methyl-4-thioxo-1*H*,3*H*-quinazolin-2-one) and/or methanolysis product, i.e. methyl *N*-(4-thiocarbamoylphenyl)carbamate. The comparison of the rate constants, β_{lg}, and ρ constants of the 2-thiocarbamoyl derivatives ($\beta_{lg} = -1.15$, $\rho = 3.1 \pm 0.1$) and 4-thiocarbamoyl derivatives ($\rho = 4.6 \pm 0.2$, $\beta_{lg} = -1.55$) shows that the ring closure reaction proceeds by the $B_{Ac}2$ mechanism with the splitting off of phenoxide anion being the rate-limiting step, while the methanolysis follows the *E*1*cB* mechanism. The ring closure reaction of 4-methoxyphenyl *N*-(2-thiocarbamoyl)-*N*-(methyl)carbamate proceeds kinetically in two steps, the respective rate constants differing by one order of magnitude. The NMR spectrum, spectral record and computational calculations of the ring closure reaction indicate that the process involves parallel reactions of two rotamers formed due to hindered rotation. Copyright © 2005 John Wiley & Sons, Ltd.
Supplementary electronic material for this paper is available in Wiley Interscience at http://www.interscience.wiley.com/jpages/0894-3230/suppmat/

KEYWORDS: *N*-(2-thiocarbamoylphenyl)carbamates; kinetics; mechanism; ring closure; rotamers

INTRODUCTION

Carbamates constitute a numerous class of organic compounds that have a number of useful properties and are applied as agrochemicals,[1] auxiliary textile agents,[2] plastics and particularly as important active pharmaceuticals for the treatment of Alzheimer disease,[3] tumours[4] and HIV.[5] Moreover, carbamates can be used in organic synthesis for protecting amino groups in syntheses of peptides and proteins.[6] An important property of some carbamates is their ability to undergo ring closure reactions. The base-catalysed ring closure is mediated by an ionisable group (usually a hydroxyl[7] or amino[8] group) that is connected with the nitrogen atom of carbamates by means of a chain or a ring. Such ring closure reactions can provide further biologically active compounds or can be made use of in the drug control release.[9–11]

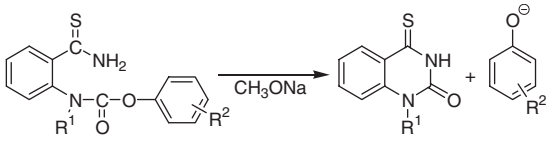
The aim of this work was to study substituent effects on the kinetics and mechanism of reactions of substituted phenyl *N*-(2-thiocarbamoylphenyl)carbamates in a basic medium.

**Correspondence to:* J. Hanusek, Department of Organic Chemistry, Faculty of Chemical Technology, University of Pardubice, Nám. Čs. legií 565, 532 10 Pardubice, Czech Republic.
E-mail: jiri.hanusek@upce.cz
Contract/grant sponsor: Ministry of Education of the Czech Republic; *Contract/grant number*: 002 162 7501.

RESULTS AND DISCUSSION

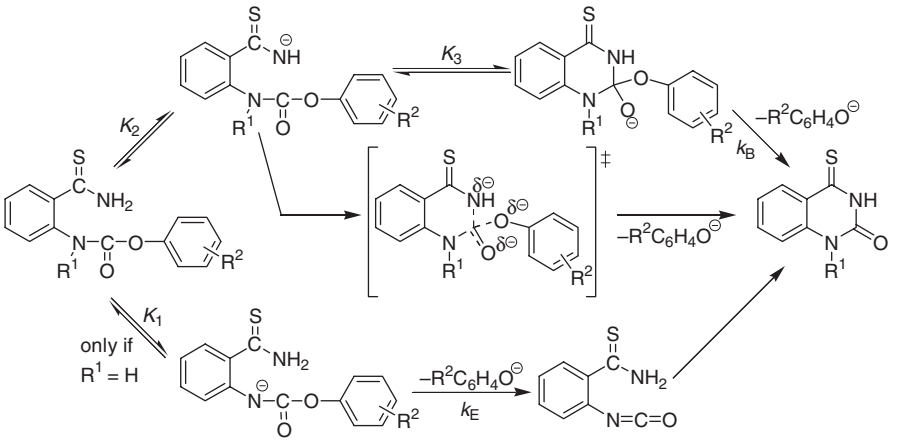
We have found that phenyl *N*-(2-thiocarbamoylphenyl)carbamates **1a**–**h**, like the analogous oxygen derivatives,[12] in basic media undergo ring closure reactions giving 4-thioxo-1*H*,3*H*-quinazolin-2-one (**2a**) or 1-methyl-4-thioxo-1*H*,3*H*-quinazolin-2-one (**2b**) (Scheme 1).

Product **2a** can be formed by three different mechanisms (Scheme 2) whose manifestation depends particularly on the nucleophilicity of the attacking nucleophilic centre (thioamide group) and on the nucleofugality of the leaving group. It has been claimed[13] that if a substituted phenoxide is the leaving group in the intermolecular reaction, then the reaction goes via isocyanate as an intermediate (*E*1*cB* mechanism). If the leaving group is an alkoxide, then an unstable tetrahedral intermediate is formed that rapidly decomposes to the final product ($B_{Ac}2$ mechanism). The third variant is a concerted mechanism involving simultaneous formation of a C—N bond and splitting of a C—O bond. However, studies of derivatives carrying an ionisable *ortho* substituent showed



	1a	1b	1c	1d	1e	1f	1g	1h	2a	2b
R^1	H	H	H	H	H	H	H	CH_3	H	CH_3
R^2	4-OCH_3	4-CH_3	H	3-OCH_3	4-Cl	3-Cl	3-NO_2	4-OCH_3	–	–

Scheme 1



Scheme 2

that the particular mechanism of ring closure does not depend solely upon the leaving group but also upon this ionisable substituent. In the cases of easily ionisable groups such as —COOH ($pK_a \approx 3$–5) and —OH ($pK_a \approx 7$–12), the $B_{Ac}2$ mechanism was proved[14,15] even if phenoxide anion was the leaving group. On the other hand, the *E*1*cB* mechanism takes place[12] if there is a weakly acidic amide group at the *ortho* position (—$CONH_2$, $pK_a \approx 15$–17). The acidity of the thioamidic group —$CSNH_2$ ($pK_a \approx 13$–15) is somewhere between those of phenols and amides, hence it could form a borderline situation between manifestations of the two mechanisms or the ring closure could go by the above-mentioned concerted mechanism. Therefore, the main attention in this paper is focused on the effect of substitution in the benzene ring of the leaving phenoxide anion.

The reaction was studied by means of UV–visible spectrophotometry in solutions of sodium methoxide (concentrations 0.01–0.5 M). The only reaction product resulting from all the phenyl *N*-(2-thiocarbamoylphenyl)-carbamates was the product of intramolecular ring closure, i.e. 4-thioxo-1*H*,3*H*-quinazolin-2-one (**2a**) or 1-methyl-4-thioxo-1*H*,3*H*-quinazolin-2-one (**2b**). Carbamate esters,[13] amides[16] and thioamides[17,18] possess carbonyl or thiocarbonyl groups highly deactivated by resonance with the adjoining nitrogen, therefore direct attack of an external nucleophile (methoxide anion) does not occur in our case. Moreover, it is well known that intramolecular reactions, especially those involving nucleophile displacements, are faster than corresponding intermolecular reactions by many orders of magnitude.[19]

Thus 4-thioxo-1*H*,3*H*-quinazolin-2-one (**2a**) can be produced by three different mechanisms, whereas **2b** by only two mechanisms (Scheme 2).

It was found that the observed rate constant at first increases steeply with increasing concentration of the base used (sodium methoxide), but above a certain concentration this increase slows and then reaches a limiting value (Fig. 1).

This course is typical of reactions with fast acid–base pre-equilibrium. The reaction obeys the general kinetic equations (1) and (2), in which k_E and k_B are the constants in the *E*1*cB* and $B_{Ac}2$ mechanisms, respectively. An analogous equation also applies to the concerted mechanism.

$$k_{obs} = \frac{k_E K_1 [CH_3ONa]}{1 + (K_1 + K_2)[CH_3ONa]} = \frac{k[CH_3ONa]}{1 + K[CH_3ONa]} \quad (1)$$

$$k_{obs} = \frac{k_B K_2 K_3 [CH_3ONa]}{1 + (K_1 + K_2)[CH_3ONa]} = \frac{k'[CH_3ONa]}{1 + K[CH_3ONa]} \quad (2)$$

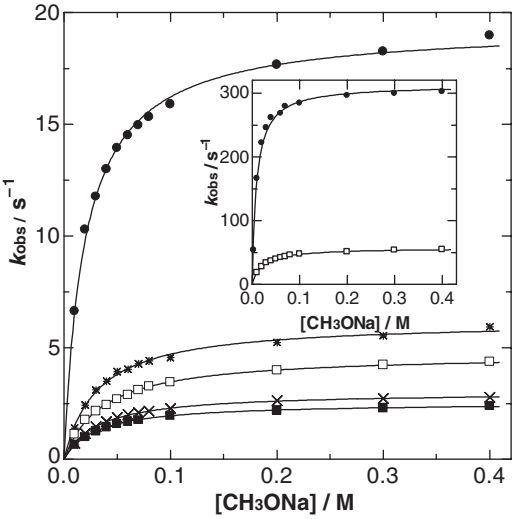


Figure 1. Dependence of observed rate constant (k_{obs}) of reaction of **1a** (■), **1b** (×), **1c** (□), **1d** (✱), **1e** (●), **1f** (inset; □) and **1g** (inset; ●) on sodium methoxide concentration

The measured data were optimised by means of Eqn (1) or (2) to provide the rate constants k (or k') and the equilibrium constants $K = K_1 + K_2$ summarised in Table 1. The curves in Fig. 1 represent the best fit of the experimental points using commercially available software. The value of K_2 can be estimated by means of the analogous *N*-methyl derivative, for which the value found was $K_2 \approx 2\ \text{M}^{-1}$, analogous with that of 2-benzoylaminothiobenzamides.[20]

By plotting the logarithms of the optimised rate constants of the ring closure reaction against the σ_m and σ_p^- constants of the individual substituents we obtained the Hammett dependence with the slope $\rho = 3.14$ (Fig. 2, closed symbols). We adopted σ_p^- constants because in the transition state of the rate-limiting step (i.e. expulsion of phenoxide anion) a partial negative charge occurs on the oxygen atom. In order to confirm this choice, we tried to prepare 4-nitrophenyl *N*-(2-thiocarbamoylphenyl)carbamate, whose σ_p and σ_p^- constants differ substantially. Unfortunately, this derivative is so unstable that it cannot be prepared in sufficient purity for kinetic measurements.

The Brønsted dependence (Fig. 3, closed symbols) of log k vs pK_a of phenols in methanol[21] gave the value

Table 1. Optimised values of rate and equilibrium constants for derivatives **1a**–**g**

Compound	k (s^{-1})	K (M^{-1})
1a	84.0 ± 0.9	33.1 ± 0.5
1b	95.8 ± 1.1	31.8 ± 0.5
1c	132 ± 3	28.0 ± 0.9
1d	198 ± 7	32.0 ± 1.5
1e	994 ± 32	51.3 ± 2.0
1f	2658 ± 52	44.6 ± 1.2
1g	33880 ± 260	106 ± 9.5

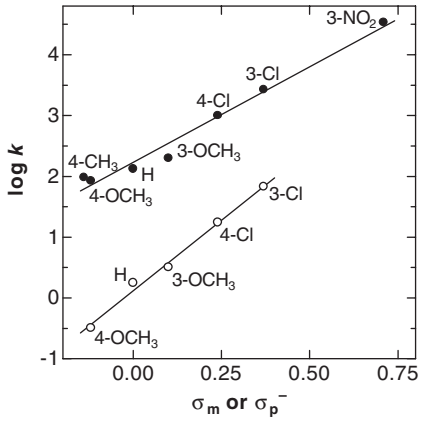


Figure 2. Hammett correlation of optimised rate constants (k) on σ_m and σ_p^- constants for **1a**–**g** (closed symbols) and for **3a**–**e** (open symbols)

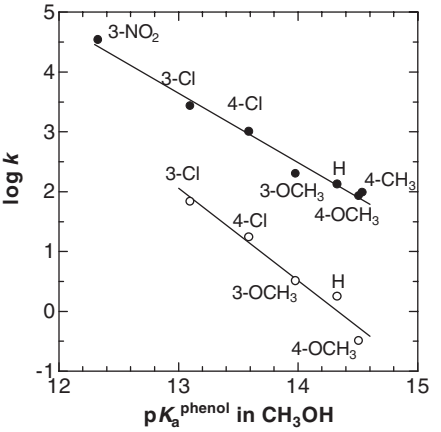
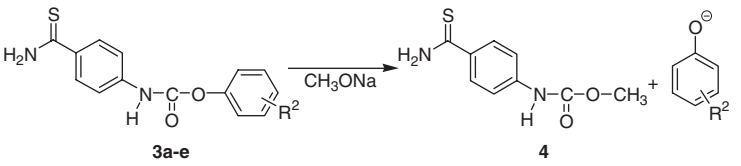


Figure 3. Brønsted correlation of optimised rate constants of **1a**–**g** (closed symbols) and **3a**–**e** (open symbols) on pK_a of leaving phenols

$\beta_{lg} = -1.15$, which also corresponds[22,23] with splitting off of phenoxide ion. To determine extent of C—O fission in the transition state it is convenient to use the normalised $\beta^{(n)}$ value given as β_{lg}/β_{eq}. We make the reasonable assumption that $\beta_{eq} = -1.8$ is the same as that for transfer of the NH_2CO— group between phenolate ion nucleophiles.[24] The calculated $\beta^{(n)} = 0.64$ means that the C—O bond in the transition step is cleaved from about 64%.

A high value of the reaction constant $\rho \approx 3$ was found[8] in intermolecular reactions following the *E*1*cB* mechanism, in which the rate-limiting step consisted in the formation of isocyanate (i.e. splitting off of phenoxide anion).

However, in our case the reaction is intramolecular and owing to the steric proximity[19] of the nucleophilic centre and carbonyl group, the tetrahedral intermediate can be rapidly formed and its decomposition to products is the rate-limiting step. This presumption is also supported by the high value of ρ and the high negative value of β.



3a-e **4**

	3a	**3b**	**3c**	**3d**	**3e**
R²	4-OCH_3	H	3-OCH_3	4-Cl	3-Cl

Scheme 3

From the above facts, it is clear that the reaction can follow either the *E*1*cB* or the $B_{Ac}2$ mechanism with rate-limiting splitting off of phenoxide anion. The concerted mechanism cannot be completely excluded either, as also in such cases the value of $\beta = -0.8$ was exceptionally found.[25]

In order to solve this problem, we focused our attention on studies of structurally similar derivatives. Therefore, a kinetic study of analogous substituted phenyl *N*-(4-thiocarbamoylphenyl)carbamates (**3a–e**) was carried out for comparison in solutions of sodium methoxide (concentrations 0.01–0.5 M); here the only product of methanolysis was methyl *N*-(4-thiocarbamoylphenyl)carbamate (**4**) (Scheme 3).

It was found by kinetic measurements that the dependences of the observed rate constant on the concentration of sodium methoxide are linear with zero intercept for all the derivatives (**3a–e**) (Fig. 4). This means that the equilibrium constant $(K_1 + K_2)[CH_3ONa] \ll 1$ and Eqn (1) or (2) is reduced to the form of Eqn (3) or (4):

$$k_{obs} = k_E K_1 [CH_3ONa] = k[CH_3ONa] \qquad (3)$$

$$k_{obs} = k_B K_2 K_3 [CH_3ONa] = k'[CH_3ONa] \qquad (4)$$

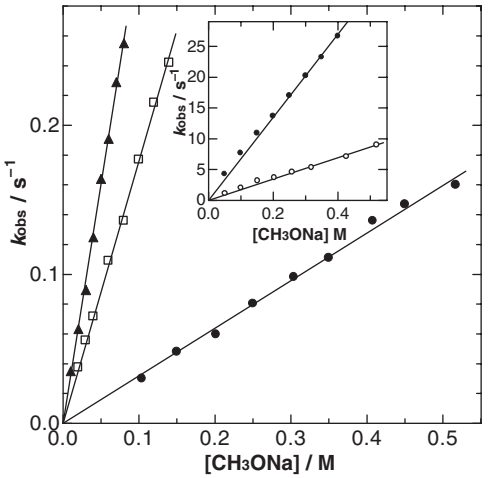
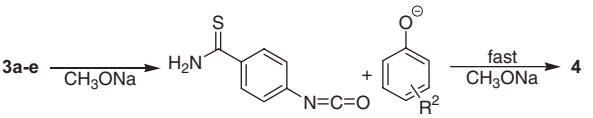


Figure 4. Dependence of observed rate constant, k_{obs} (s^{-1}) on concentration of sodium methoxide [CH_3ONa] (M) for compounds **3a** (●), **3b** (□), **3c** (▲), **3d** (inset; ○) and **3e** (inset; ●) on sodium methoxide concentration

By plotting the Hammett equation for these bimolecular rate constants (k) obtained from the slopes of plots of k_{obs} vs [CH_3ONa], we obtained a linear dependence (Fig. 2, open symbols), whose slope value of 4.6 ± 0.2 indicates that the *E*1*cB* mechanism is operating (Scheme 4) and $k = k_E K_1$. Slow formation of isocyanate and its fast reaction with methoxide ion is in accordance with the literature[25,26] and is also supported by a higher $\beta_{lg} = -1.55$ (Fig. 3, open symbols). We also calculated extent of C—O fission in the transition state using the normalised $\beta^{(n)}$ value [$\beta^{(n)} = \beta_{lg}/\beta_{eq}$; $\beta_{eq} = -1.8$].[24] The calculated $\beta^{(n)} = 0.86$ means that the C—O bond is cleaved in the transition step in to a larger extent (by about 86%) than in the case of **1a–g**. The values of the bimolecular rate constants are given in Table 2.

From the comparison of rate constants of the *ortho* and *para* derivatives, it follows that in the case of the *ortho* derivative, both the reaction rate and acidity are distinctly increased and the ρ constant is much lower. It has been stated[27] that, provided the same mechanism operates, the rate constants of reactions of *ortho* derivatives are about eight times as high, but in our case the increase is much greater (about two orders of magnitude). This means that, in contrast to compounds **3a–e**, in the case of **1a–g** the *E*1*cB* mechanism does not operate; instead, the $B_{Ac}2$ mechanism operates with rate-limiting removal of phenoxide ion or the concerted mechanism. The high ρ value for **1a–g** can be explained as follows. Both K_2 and k_B show $\rho > 0$. The



Scheme 4

Table 2. Optimised values of rate constants for derivatives **3a–d**

Compound	k ($M^{-1} \cdot s^{-1}$)
3a	0.32 ± 0.01
3b	1.76 ± 0.01
3c	3.21 ± 0.03
3d	17.3 ± 0.3
3e	67.6 ± 0.9

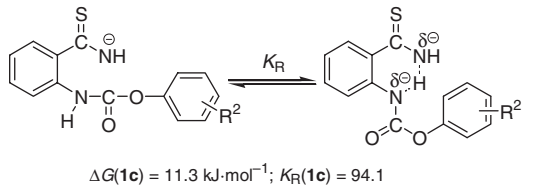


Figure 5. Intramolecular hydrogen bond in phenyl *N*-(2-thiocarbamoylphenyl)carbamates **1a**–**g**

equilibrium constant for the formation of a cyclic tetrahedral intermediate should give ρ near zero since electron withdrawal from R^2 should render NH^- less negative but should render $C{=}O$ more positive. Hence a high ρ value should be expected for both $B_{Ac}2$ (**1a**–**g**) and for $E1cB$ (**3a**–**e**).

The strong decrease in acidity ($K_1 + K_2$) of the *para* derivatives can be explained by the existence of an intramolecular hydrogen bond in the *ortho* derivative, in a similar way[20] as in the case of 2-benzoylaminothiobenzamides. Also, computational study of the conjugated base of **1c** shows that there exist two stable rotamers (Fig. 5) differing in Gibbs energy by about 11.3 kJ · mol^{-1}.

In order to obtain further information, we followed the kinetic behaviour of the ring closure reaction of 4-methoxyphenyl *N*-(2-thiocarbamoylphenyl)-*N*-(methyl)-carbamate (**1h**) under the same conditions as above. On measuring the reaction rate of **1h**, it was found that the absorbance–time dependence is no longer single exponential (Fig. 6). The reaction proceeds kinetically in two steps, the rate constants of which differ by about one order of magnitude.

However, this is not a consecutive reaction of the type substrate → stable intermediate → product, because the spectral recording shows a sharp isosbestic point (Fig. 7).

If the case were a consecutive reaction sequence, such a stable intermediate could only be the tetrahedral intermediate; however, its absorption spectrum would lie in

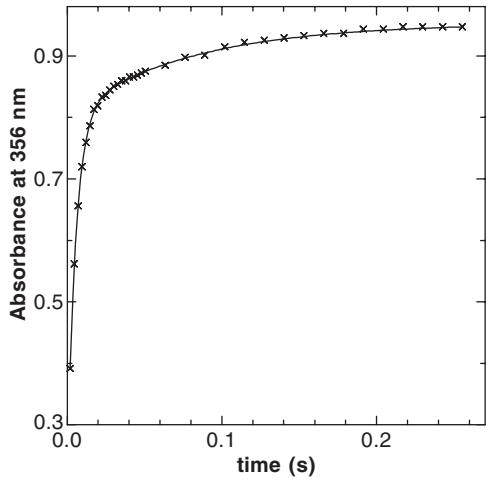


Figure 6. Kinetic curve for derivative **1h** at 356 nm obtained in 0.1 M CH_3ONa solution

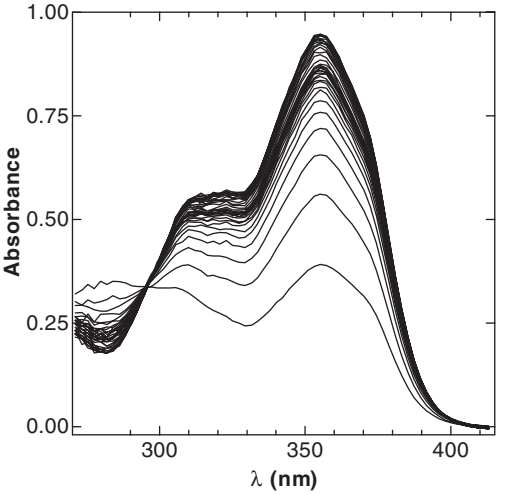


Figure 7. Spectral recording of reaction of derivative **1h** obtained in 0.1 M CH_3ONa solution

the region of lower wavelengths and no isosbestic point would be formed. In addition, it is known that the lifetimes of negatively charged tetrahedral intermediates are in most cases very short.[28,29]

The ^{1}H NMR spectrum of **1h** reveals that owing to hindered rotation[30] the compound exists in solution in two unequally populated forms (*I* and *II*) in the ratio 3:4 or 4:3; conjugated bases of these forms undergo ring closure reactions at different rates (Scheme 5). A similar case was described[31] also in the ring closure of structurally cognate *N*-methyl-*N*-phenylamides.

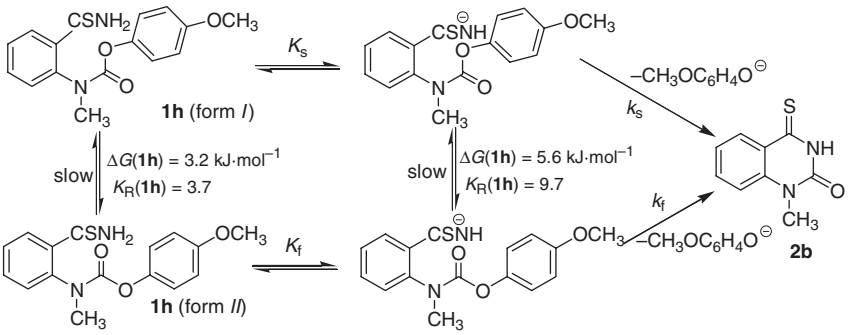
This result is also supported by the fact that the observed rate constants (k_{obs}^{fast} and k_{obs}^{slow}) of the two reactions are dependent on sodium methoxide concentration (Fig. 8). Their values were determined from Eqn (5) using commercially available software.[32]

$$A_t - A_\infty = Me^{-k_{obs}^{fast}t} + Ne^{-k_{obs}^{slow}t} \quad (5)$$

Another possibility could be the variant in which only one of the forms undergoes the ring closure reaction, whereas the other is not cyclised at all, but is slowly converted into the first form. In such a case, however, the rate of such transformation of the two forms would be independent of the sodium methoxide concentration.

Moreover, the computational study of anion of **1h** shows that this species also exists in two unequally populated forms differing in Gibbs energy by only about 3.2 kJ · mol^{-1} (5.6 kJ · mol^{-1} for anions). However, the calculated energy barriers between *I* and *II* and also between their anions are very high ($\Delta G \approx 76$ and 92 kJ · mol^{-1}, respectively), so that interconversion of these two forms is very slow.

The two dependences of observed rate constants on sodium methoxide concentration have the form typical of a rapid pre-equilibrium (Fig. 8). This reaction can only proceed via a concerted mechanism or $B_{Ac}2$ (Scheme 2).



Scheme 5

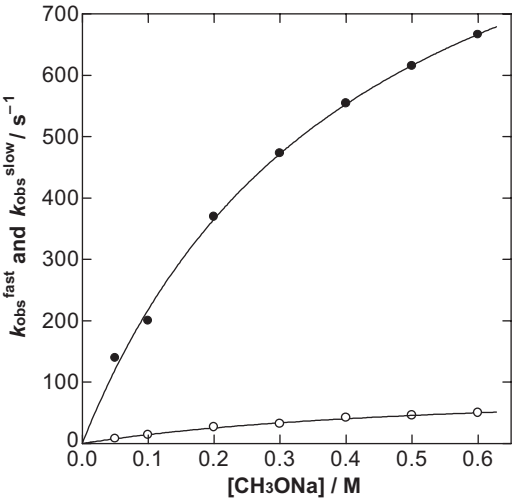


Figure 8. Dependence of observed rate constants of parallel formation of **2b** from both forms (*I* and *II*) of compound **1h** (○, slower reaction; ●, faster reaction)

The *E*1*cB* mechanism is excluded owing to the impossibility of formation of the carbamate anion. Optimisation of the data measured by means of Eqn (2) gave values of the rate and equilibrium constants k_f, k_s, K_f and K_s (Table 3).

The equilibrium constants K_f and K_s obtained for derivative **1h** are ~15 times lower than the corresponding value for derivative **1a**, while the rate constant k_s is almost the same and k_f is 13.5 times higher. The much higher value of K(**1a**) results from the fact that the anion stabilised by the presence of intramolecular hydrogen bond is more abundant (Fig. 5). The much lower rate constant of **1a** compared with k_f(**1h**) results from the fact that only the less abundant anion (which is not stabilised by hydrogen bonding) can undergo the ring closure reaction. In the case of **1h**, stabilisation of the anion by hydrogen bonding is impossible, but owing to the hindered rotation around the C—N bond there exist two forms, which cyclise at different rates (Scheme 5).

From all the findings given, it can be deduced that all the *ortho* derivatives react by the $B_{Ac}2$ mechanism with rate-limiting removal of phenoxide ion.

Table 3. The values of optimised constants for slower and faster cyclisation of **1h**

Parameter[a]	Value
k_f [s^{-1}]	1133 ± 63
K_f [M^{-1}]	2.38 ± 0.25
k_s [s^{-1}]	97.5 ± 7.18
K_s [M^{-1}]	1.78 ± 0.31

[a] Subscripts f and s denote faster and slower reaction, respectively.

EXPERIMENTAL

Kinetic procedures. The kinetic measurements were carried out on an Hewlett-Packard Model 8453 diode-array UV–visible spectrophotometer in 1 cm closable cells at 25 °C. The cell was always charged with 1 ml of sodium methoxide solution and, after attaining the chosen temperature, 10 µl of a methanolic solution of the substrate **3a–c** were added so that the resulting substrate concentration would be about 5×10^{-4} M. The measurements of reactions with half-lives below 2 s (**1a–h**, **3d–e**) were carried out using a diode-array stopped-flow SX.18 MV-R instrument (Applied Photophysics). The observed pseudo-first-order rate constants k_{obs} were calculated from the measured time dependences of absorbance with the help of an optimisation program.[32]

Computational details. The structures of **1c** and **1h** and their anions were optimised at the B3LYP[33,34]/TZVP[35] level. The nature of these structures was characterised by means of the correct number of negative eigenvalues in the exact Hessian. Solvent effects were computed for the gas-phase geometries at the same theoretical level by means of the PCM model[36] using the default options (solvent methanol).

Materials. 2-Aminothiobenzamide and 2-methylaminothiobenzamide were prepared according to the literature.[37] Substituted phenyl *N*-(thiocarbamoylphenyl)carbamates were prepared according to the general procedure described in the supplementary material, available in Wiley Interscience.

Acknowledgement

This work was supported by the Ministry of Education of the Czech Republic (Project No. 002 162 7501).

REFERENCES

1. (a) Plimmer JR (ed). *Encyclopedia of Agrochemicals*, 3 Volume Set. Wiley-VCH: Weinheim, 2003; (b) Motolcsy G, Nadasy M, Andriska V. In *Pesticide Chemistry*; Akadémiai Kiadó: Budapest, 1988; 90.
2. Mikolajczyk W, Wawro D, Struszczyk H. *Fibres Text. East. Eur.* 1998, **6**: 53–55. *Chem. Abstr.* 1999; **130**: 4757c.
3. Mustazza C, Borioni A, Del Giudice MR, Gatta F, Ferretti R, Meneguz A, Volpe MT, Lorenzini P. *Eur. J. Med. Chem.* 2002; **37**: 91–109.
4. Ray S, Chaturvedi D. *Drugs Future* 2004; **29**: 343–357.
5. Chang SL, Griesgraber G, Abraham TW, Garg T, Song H, Zimmerman CL, Wagner CR. *Nucleosides Nucleotides Nucleic Acids* 2000; **19**: 87–100.
6. Lloyd-Wiliams P, Alberico F, Giralt E. *Chemical Approaches to Synthesis of Peptides and Proteins*. CRC Press: Bocca Raton, FL, 1997.
7. Maleski RJ, Osborne CE, Cline SM. *J. Heterocycl. Chem.* 1991; **28**: 1937–1939.
8. Hegarty AF, Frost LN. *J. Chem. Soc., Perkin Trans. 2* 1973; 1719–1728.
9. Thomsen KF, Bundgaard H. *Int. J. Pharm.* 1993; **91**: 39–49.
10. Shan D, Nicolaou MG, Borchardt RT, Wang B. *J. Pharm. Sci.* 1997; **86**: 765–767.
11. D'Souza AJM, Topp EM. *J. Pharm. Sci.* 2004; **93**: 1962–1979.
12. Hegarty AF, Frost LN, Coy JH. *J. Org. Chem.* 1974; **39**: 1089–1093.
13. Adams P, Baron FA. *Chem. Rev.* 1965; **65**: 567–602.
14. Frost LN, Hegarty AF. *J. Chem. Soc., Chem. Commun.* 1973; 82–83.
15. Hutchins JEC, Fife TH. *J. Am. Chem. Soc.* 1973; **95**: 2282–2286.
16. Challis BC, Challis JA. In *The Chemistry of Amides*, Zabicky J (ed). Interscience: London, 1970.
17. Mollin J, Labodová A. *Collect. Czech. Chem. Commun.* 1977; **42**: 517–523.
18. Pesters OM, De Ranter CJ. *J. Chem. Soc., Perkin Trans. 2* 1976; 1062–1065.
19. Kirby AJ. *Adv. Phys. Org. Chem.* 1980; **17**: 183–278.
20. Hanusek J, Sedlák M, Šimůnek P, Štěrba V. *Eur. J. Org. Chem.* 2002; 1855–1863.
21. Rived F, Rosés M, Bosch E. *Anal. Chim. Acta* 1998; **374**: 309–324.
22. Williams A. *J. Chem. Soc., Perkin Trans. 2* 1972; 808–812.
23. Williams A. *J. Chem. Soc., Perkin Trans. 2* 1973; 1244–1247.
24. Al-Rawi H, Williams A. *J. Am. Chem. Soc.* 1977; **99**: 2671–2678.
25. Štěrba V, Hrabík O, Kaválek J, Mindl J, Williams A. *Org. Biomol. Chem.* 2003; **1**: 415–421.
26. Hegarty AF, Frost LN, Scott FL. *J. Chem. Soc., Perkin Trans. 2* 1975; 1166–1171.
27. Hegarty AF, Frost LN. *J. Chem. Soc., Chem. Commun.* 1972; 500–501.
28. McClelland RA, Santry LJ. *Acc. Chem. Res.* 1983; **16**: 394–399.
29. Adler M, Adler S, Boche G. *J. Phys. Org. Chem.* 2005; **18**: 193–209.
30. Macháček V, Večeřa M. *Collect. Czech. Chem. Commun.* 1972; **37**: 2928–2932.
31. Macháček V, Hassanien MMM, Štěrba V. *J. Chem. Soc., Perkin Trans 2* 1986; 813–817.
32. *!Pro-K Global Analysis and Simulation Software, Version 4.21*. Applied Photophysics: Leatherhead, 2000.
33. Lee C, Yang W, Parr R. *Phys. Rev. B: Condens. Matter* 1988; **37**: 785–789.
34. Becke AD. *J. Chem. Phys.* 1993; **98**: 5648–5652.
35. Schaefer A, Huber C, Ahlrichs R. *J. Chem. Phys.* 1994; **100**: 5829–5835.
36. Cossi M, Barone V, Mennucci B, Tomasi J. *Chem. Phys. Lett.* 1998; **286**: 253–260.
37. Hanusek J, Hejtmánková L, Kubicová L, Sedlák M. *Molecules* 2001; **6**: 323–337.