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Kinetics and mechanism of the reaction of substituted *O*-benzoylbenzamidoximes with sodium methoxide in methanol

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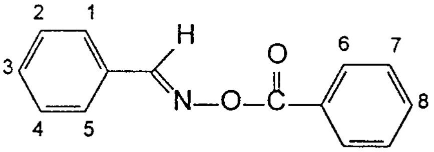
ABSTRACT: The kinetics of reaction of substituted *O*-benzoylbenzamidoximes with sodium methoxide in methanol were studied at 25 °C. The only reaction products are substituted benzamidoximes and methyl benzoates. The slope of the dependence of rate constant on sodium methoxide concentration gradually increases, but in the presence of C_{18} crown ether the dependence becomes linear and the rate constant is lower than in the absence of the crown ether, which means that the reaction is catalysed by sodium cation. The rate constants of reactions with the ion pair and with methoxide ion were determined with the presumption that the rate-limited step of the catalysed reaction is the reaction of substituted *O*-benzoylamidoximes with the ion pair of sodium methoxide. The rate constants of the reaction with the ion pair are about 20 times higher than those of the non-catalysed process. The slopes of the dependence of log k of the non-catalysed and catalysed reactions on the pK_a of substituted benzamidoximes are 1.05 and 0.94, respectively. These high values indicate the rate-limiting step involving the splitting off of substituted benzamidoxime from the tetrahedral intermediate. On the basis of the relatively high ρ constant of methanolysis at the benzoyl group substituted derivatives (2.17 and 1.98 for the non-catalysed and catalysed reactions, respectively), it can be presumed that the transition state structure will be close to the tetrahedral intermediate. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: *O*-benzoylbenzamidoximes; methanolysis kinetics; sodium cation catalysis

INTRODUCTION

Substituted arylbenzamidoxime carbonates undergo cyclization in aqueous hydroxides or in aprotic solvents to give 3-aryl-1,2,4-oxadiazol-5-ones,[1,2] but their reaction with sodium methoxide in methanol exclusively results in a two-step methanolysis giving phenolate salts, benzamidoximes and dimethyl carbonate.[3] In addition to the reaction with methoxide ion there also takes place a reaction with sodium methoxide ion pair which is one order of magnitude faster, and the methanolysis proceeds via a concerted mechanism.[3] Also, *O*-benzoylbenzamidoximes (**1**) are cyclized in aqueous alkali metal hydroxides and aprotic solvents to give 3,5-diaryl-1,2,4-oxadiazole derivatives.[5–8] The aim of this work was to find out whether compounds **1** reacting with sodium methoxide in methanol only undergo methanolysis as aryloxime carbonates and whether the reaction is catalysed by sodium cation, and to suggest a reaction mechanism.



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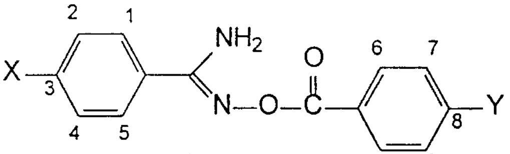

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a: X = OMe; Y = H
b: X = H; Y = H
c: X = Cl; Y = H
d: X = NO_2; Y = H
e: X = H; Y = OMe
f: X = H; Y = Cl
g: X = H; Y = NO_2

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Table 1. Melting-points, yields of syntheses and elemental analyses of substituted *O*-benzoylbenzamidoximes **1a–g** and *O*-benzoylbenzaldoxime (**2**)

Compound	M.p. (°C)	Yield (%)	Formula (MW)	Calculated/found (%)[a] C	H	N
1a	145–148	80	$C_{15}H_{14}N_2O_3$	66.66	5.22	10.36
	(146–148)[13]		(270.3)	66.99	5.30	10.33
1b	149–151	57	$C_{14}H_{12}N_2O_2$	69.99	5.03	11.66
	(148)[14]		(240.3)	69.52	5.00	11.44
1c	172–174	50	$C_{14}H_{11}N_2O_2Cl$	61.21	4.04	10.20
	(175)[14]		(274.7)	61.47	3.96	9.96
1d	198–200	51	$C_{14}H_{11}N_3O_4$	58.95	3.89	14.73
	(164–166)[10]		(285.3)	58.99	3.85	14.58
1e	149–151	50	$C_{15}H_{14}N_2O_3$	66.66	5.22	10.36
	(146–148)[15]		(270.3)	66.67	5.26	10.39
1f	178–180	80	$C_{14}H_{11}N_2O_2Cl$	61.21	4.04	10.20
	(174)[15]		(274.7)	61.47	3.96	9.96
1g	199–201	97	$C_{14}H_{11}N_3O_4$	58.95	3.89	14.73
	(202–203)[10]		(285.3)	58.60	3.81	14.66
2	101–102	43	$C_{14}H_{11}NO_2$	74.65	4.92	6.22
	(101–102)[11]		(225.3)	74.74	4.91	6.21

[a] Calculated values in first row, found values in second row.

Table 2. ^{1}H NMR spectra of substituted *O*-benzoylbenzamidoximes **1a–g** and *O*-benzoylbenzaldoxime (**2**)

Compound	H-1,5 (m)	H-2,(3),4 (m)	H-6,10 (m)	H-7,(8),9 (m)	NH_2 (s)	Other positions
1a	6.90–6.92	7.68–7.71	8.06–8.08	7.44–7.48 (7.55–7.59)	5.16	3.82 s (OMe)
1b	7.37–7.47 (5H)		8.05–8.07	7.71–7.74 (7.55–7.59)	5.26	—
1c	7.60–7.62	7.84–7.86	8.23–8.25	7.57–7.61	7.10	—
1d	8.24–8.27	7.58–7.63 (7.71–7.73)	8.38–8.40	8.09–8.12	7.31	—
1e	7.79–7.82	7.50–7.57	8.19–8.21	7.09–7.11	6.97	3.82 s (OMe)
1f	7.42–7.50 (5H)		8.02–8.04	7.74–7.76	5.12	—
1g	7.81–7.84	7.54–7.59	8.48–8.51	8.38–8.41	7.17	—
2	7.44–7.51 (5H)		8.11–8.14	7.79–7.81	—	—

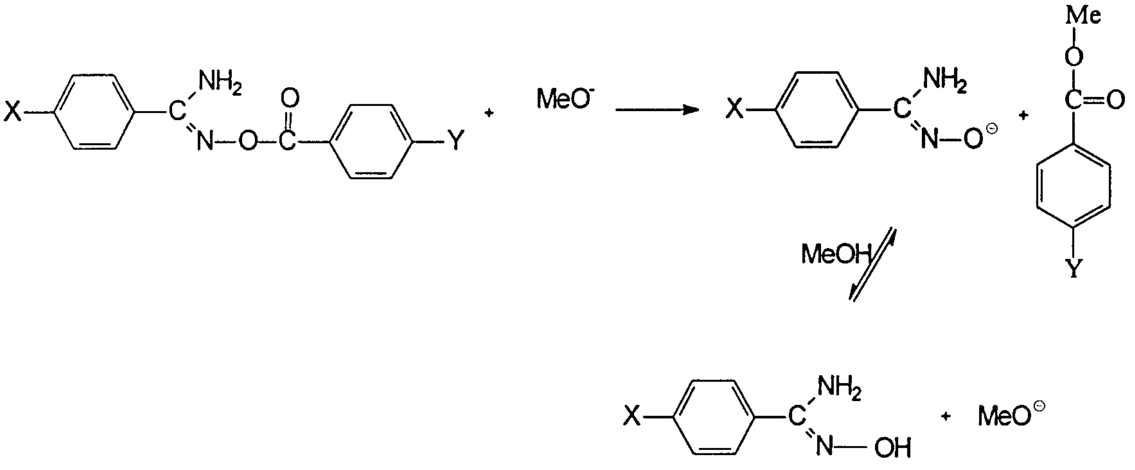
Table 3. Rate constants k_{ip} (s^{-1} mol^{-1} dm^3), k_i and $k_{iC_{18}}$ (s^{-1} mol^{-1} dm^3) of the methanolysis of *O*-benzoylbenzamidoximes **1a–g** measured at 25 °C at the wavelengths λ_{anal} (nm) in methanolic solutions of sodium methoxide with or without the addition of C_{18} crown ether and the pK_a values of the respective benzamidoximes in the same medium

Compound	$k_i \times 10$	$k_{iC_{18}} \times 10$	k_{ip}	λ_{anal}	pK_a[a]
1a	0.521 ± 0.071	0.578 ± 0.012	1.467 ± 0.069	270	16.83 ± 0.03
1b	0.802 ± 0.049	0.787 ± 0.036	1.599 ± 0.033	300	16.67 ± 0.02
1c	1.069 ± 0.092	1.186 ± 0.075	2.538 ± 0.086	264	16.48 ± 0.03
1d	3.487 ± 0.352	3.345 ± 0.055	6.556 ± 0.346	300	16.10 ± 0.02
1e	0.156 ± 0.030	0.144 ± 0.071	0.384 ± 0.018	280	—
1f	3.199 ± 0.374	3.343 ± 0.097	4.305 ± 0.360	266	—
1g	35.599 ± 3.942	34.077 ± 2.072	57.122 ± 6.845	300	—

[a] Ref. 3.

EXPERIMENTAL

4,4′-Substituted *O*-benzoylbenzamidoximes **1a**–**g** were obtained by acylation of the corresponding benzamidoximes[9,10] prepared by reactions of the respective benzonitriles with hydroxylamine in aqueous alcohol.[1] *O*-Benzoylbenzaldoxime (**2**) was obtained by acylation of benzaldoxime[11] obtained by reaction of benzaldehyde with hydroxylamine in aqueous sodium acetate.[12] The purity of all the substances synthesized was checked by



Scheme 1.

their melting-points and elemental analyses (Table 1). The structure of the compounds prepared was confirmed by ^{1}H NMR spectroscopy (Table 2).

The melting-points were measured on a Kofler apparatus and were not corrected. Electron spectra were measured on a Hewlett-Packard 8453 diode-array instrument at 25 °C. ^{1}H NMR spectra were measured on a Bruker AMX 360 spectrometer at 360.14 MHz at 25 °C in deuterochloroform. The chemical shifts are referenced to the signals of the non-deuterated solvent [δ (^{1}H) 7.25, $CHCl_3$]. The identification of the reaction products and intermediates was carried out on a Waters 616 liquid chromatograph combined with a VG-Platform Fison-ESP-3000Da spectrometer.

Kinetic measurements. A 1 cm quartz cell with a lid placed in the thermostated compartment of the spectrophotometer was charged with 2 ml of methanolic sodium methoxide (5×10^{-3} –1.4×10^{-1} mol l^{-1}). In the experiments with C_{18} crown ether, the concentration of the latter was always 2×10^{-3} mol l^{-1} higher than that of sodium methoxide. Then 10–20 μl of a methanolic solution of substrate **1** or **2** (1×10^{-2} mol l^{-1}) was injected, and after mixing the absorbance of the mixture was measured at 260 nm (**2**) or at the λ_{anal} wavelengths given in Table 3 (**1a–g**).

RESULTS AND DISCUSSION

Catalytic effect of sodium cation

The reaction of sodium methoxide with *O*-benzoylbenzamidoximes **1a–g** in methanol results exclusively in methanolysis, giving substituted benzamidoximes and methyl esters of substituted benzoic acids (Scheme 1).

Amidoximes can exist in two configurations, *E* and *Z*. *N*,*N*-Dialkylamidoximes exist in both configurations and they were also isolated in some cases. The equlibrium lies entirely on the side of the *E* configuration.[16–18] Amidoximes with a free amino group or one alkyl group only are in the *Z* configuration. The *E* configuration has never been isolated.[14,19] The stability of the *Z* form could arise from steric effects but the presence of an internal H-bond, which has been observed in crystalline structure studies, is also a major factor.[19] Attempts to convert the *Z* into the *E* configuration photochemically failed, maybe because the *E* form, once formed, can convert rapidly to the *Z* form via a prototropic shift, which is not possible in *N*, *N*-dialkyl derivatives.[18,19] In the case of substituted *O*-benzoyl-*N*, *N*-dialkylbenzamidoximes, only the *E* isomers were isolated and measured in solution.[18] *O*-Benzoyl derivatives with a free amino group exist in the *Z* configuration.[14]

The reaction kinetics were studied in a large excess of sodium methoxide, hence the methanolysis proceeded kinetically as a reaction of pseudo-first order. The slopes of the dependence of observed rate constants k_{obs} (s^{-1}) on sodium methoxide concentration showed an increasing trend in all cases (Fig. 1), although the transition state does not allow the participation of a second methoxide ion.

In the presence of a small surplus of crown ether, the dependence of k_{obs} on methoxide concentration was linear (Fig. 2) and the k_{obs} values always were lower than the corresponding values obtained in the absence of the crown ether. This can be interpreted by catalytic participation of sodium ion in the methanolysis of the substrate, similar to the methanolysis of arylbenzamidoxime carbonates.[3]

The gradually increasing slope of the dependence of k_{obs} on sodium methoxide concentration can be explained by parallel reactions of the substrate with methoxide anion and with the ion pair (which is more reactive than the anion alone) (Scheme 2).

In Scheme 2, k_i and k_{ip} are rate constants of reactions of the substrate with the anion and with the ion pair, respectively, and K_{ip} (= 7.5)[20] is the equilibrium constant

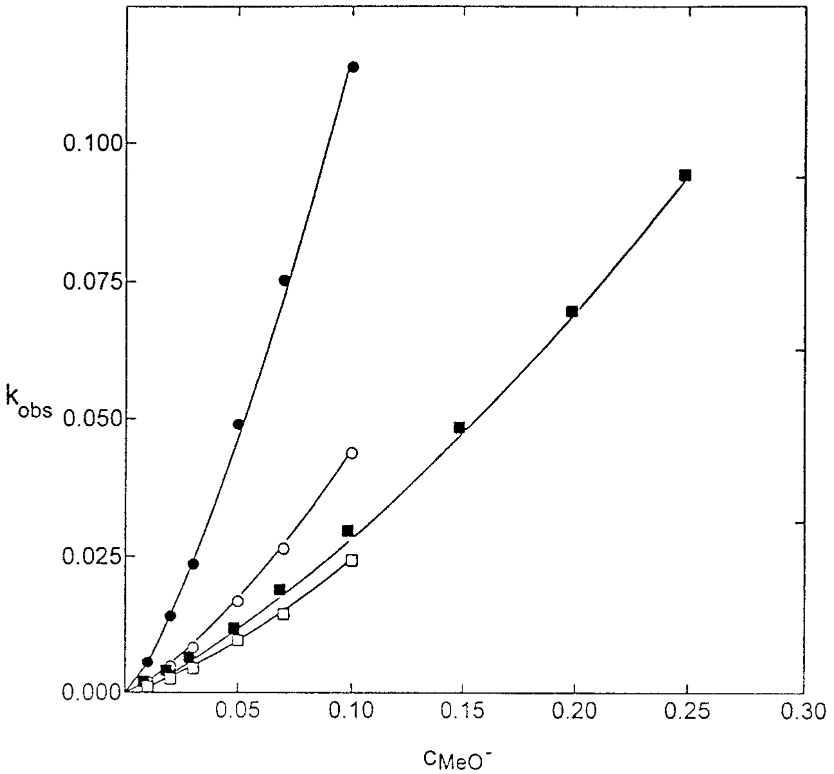


Figure 1. Dependence of observed rate constants k_{obs} (s^{-1}) of methanolysis of (□) **1a**, (■) **1b**, (○) **1c** and (●) **1d** on sodium methoxide concentration c_{MeO^-}(mol l^{-1}) in the absence of C_{18} crown ether. Experimental points are shown together with theoretical curves calculated from Eqn. (3)

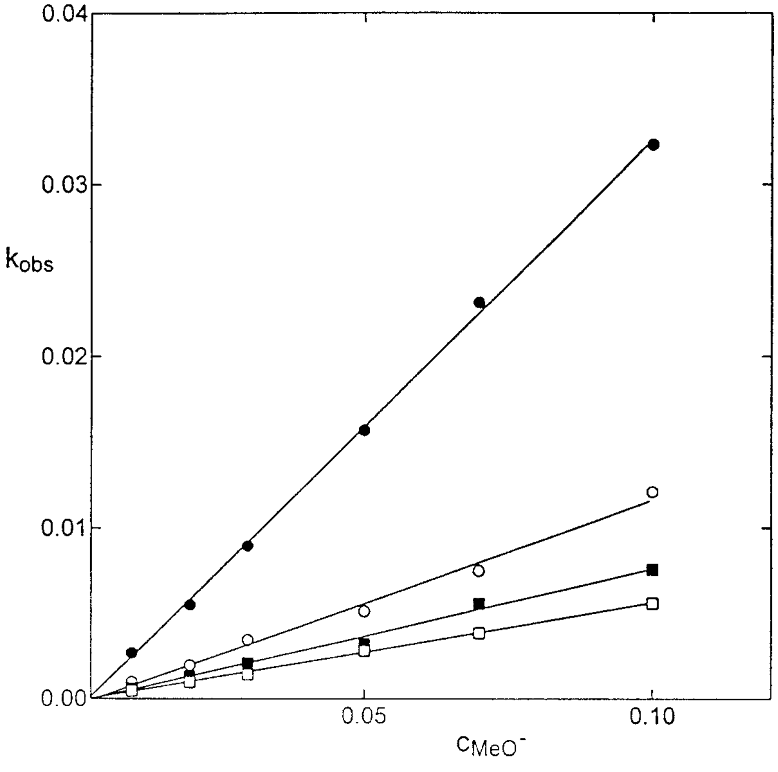
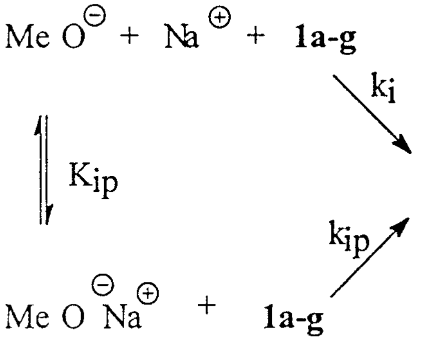


Figure 2. Dependence of observed rate constants k_{obs} (s^{-1}) of methanolysis of (□) **1a**, (■) **1b**, (○) **1c** and (●) **1d** on sodium methoxide concentration c_{MeO^-} (mol l^{-1}) in the presence of C_{18} crown ether



Scheme 2.

of association of Na^+ cation with MeO^- anion:

$$K_{ip} = \frac{[\mathrm{MeONa}]}{[\mathrm{MeO^-}][\mathrm{Na^+}](\gamma_\pm)^2} = \frac{[\mathrm{MeONa}]}{[\mathrm{MeO^-}]^2(\gamma_\pm)^2} \qquad (1)$$

The activity coefficient of the ion pair is presumed to be equal to 1, hence the activity of the ion pair is equal to its concentration. The activity coefficients of sodium and methoxide ions were obtained from the equation[21]

$$-\log \gamma_\pm = \frac{1.69\sqrt{I}}{1 + 2.5\sqrt{I}} \qquad (2)$$

The observed rate constant in the absence of crown ether is given by

$$\begin{aligned} k_{obs} &= k_i[\mathrm{MeO^-}] + k_{ip}[\mathrm{MeONa}] \\ &= k_i[\mathrm{MeO^-}] + k_{ip}K_{ip}[\mathrm{MeO^-}]^2(\gamma_\pm)^2 \end{aligned} \qquad (3)$$

The actual concentration of methoxide ion was calculated with the equation

$$[\mathrm{MeO^-}] = \frac{-1 + \sqrt{1 + 4c_{\mathrm{MeO^-}}K_{ip}(\gamma_\pm)^2}}{2K_{ip}(\gamma_\pm)^2} \qquad (4)$$

The dependence of $k_{obs}/[MeO^-]$ on K_{ip} $[MeO^-]$ $(\gamma_\pm)^2$ is linear with slope k_{ip} and intercept k_i (Fig. 3). The values of k_i and k_{ip} (Table 3) were calculated by multiple non-linear regression using Eqn. (3).

The k_i values obtained from the measurements in the presence of the crown ether are also presented in Table 3.

In the case of methanolysis of carbonates,[3] for the reaction with an ion pair the presence of an NH_2 group was necessary and in order to prove this in the case of the substrates studied here, we determined the rate constant of the reaction of **2** with methoxide both in the presence and in the absence of the crown ether. In both the cases the dependence of k_{obs} on methoxide concentration was linear and the k_{obs} values were equal at equal methoxide concentrations ($k_i = 3.60 \pm 0.17$ and $k_{iC_{18}} = 3.53 \pm 0.14$

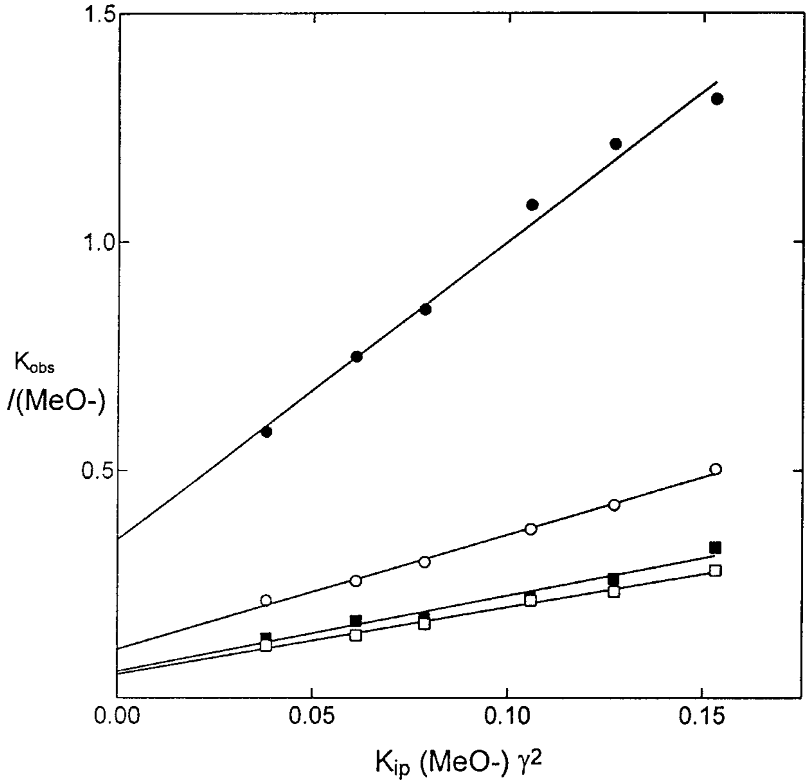
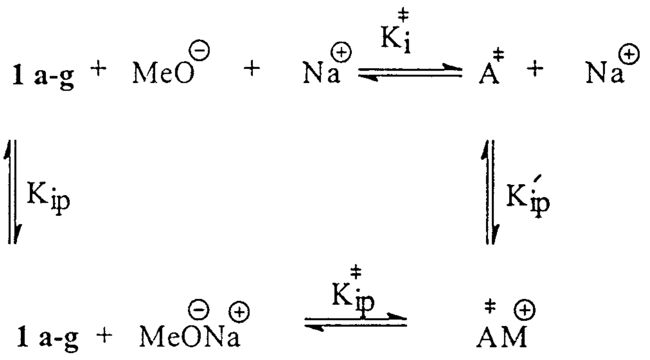


Figure 3. Dependence of $k_{obs}/[MeO^-]$ on K_{ip} $[MeO^-]$ $(\gamma_\pm)^2$ with slope k_{ip} and intercept k_i for methanolysis of *O*-benzoylbenzamidoximes (□) **1a**, (■) **1b**, (○) **1c** and (●) **1d**



Scheme 3.

s^{-1} mol^{-1} dm^3, λ_{anal} = 260 nm). We presume that for **1a–g** there takes place a complex formation of the sodium cation of the ion pair with the oxygen atom of the carbonyl group and the electron pair of the partially negatively charged, doubly bonded nitrogen atom, as in the case of arylbenzamidoxime carbonates.

According to the transition state theory, the kinetic data can be divided into a contribution of stabilization by sodium cation in the starting (ground) state and in the transition state. The degree of stabilization of the activated complex can be evaluated by the method developed by Kurz[22–24] (Scheme 3).

$K^\ddagger_{ip}$ and $K^\ddagger_{ip}$ are the equilibrium constants of the catalysed and non-catalysed formation of the activated complexes $A^\ddagger$ and $A^\ddagger M^+$, respectively, and K'_{ip} is the association constant of formation of the complex of the sodium ion with the transition state A‡ of the non-catalysed reaction. On the basis of the respective thermodynamic cycle, it is possible to calculate this virtual association constant.

Since, according to the activated complex theory, the concentrations of activated complexes are in equilibrium with those of reactants and, at the same time, both starting ions are in equilibrium with the ion pair, the two activated complexes are also in equilibrium, although there is no direct dynamic equilibrium between them.[22]

For a rate constant we can write

$$k = \frac{kT}{h} e^{\frac{-\Delta G^\ddagger}{RT}} = \frac{kT}{h} K^\ddagger \qquad (5)$$

so that K'ip can be calculated from

$$K'_{ip} = \frac{k_{ip} K_{ip}}{k_i} \qquad (6)$$

The change in the Gibbs energy, δG_{ip}, of formation of the ion pair was calculated from

$$-\delta G_{ip} = RT \ln K_{ip} \qquad (7)$$

The catalysis takes place if the metal cation stabilizes the activated complex more than the ground state (Fig. 4). In the opposite case inhibition occurs. The resulting

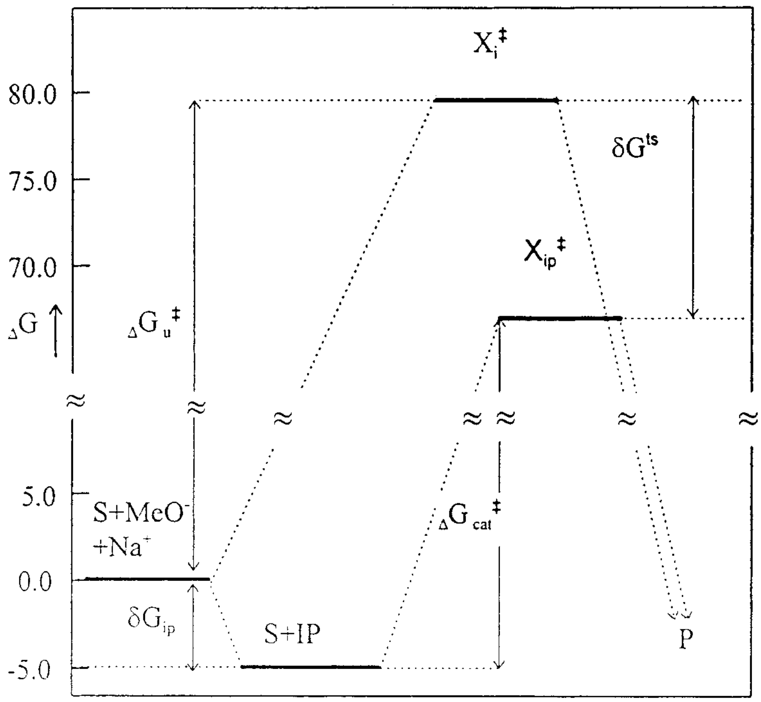
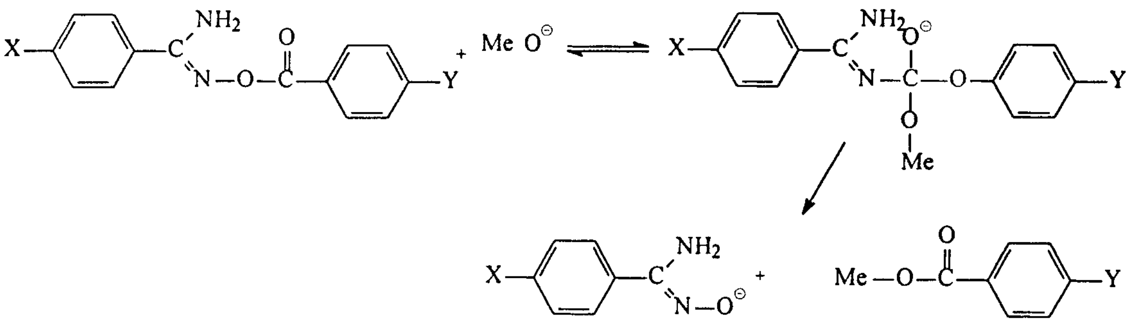


Figure 4. Relative changes in Gibbs energies (kJ mol^{-1}) of the species indicated for methanolysis of *O*-benzoylbenzamidoxime **1b** referenced to the zero energy level of starting reactants



Scheme 4.

catalytic effect ΔG_{cat} is given by

$$\begin{aligned}\Delta G_{cat} &= \Delta G^{\ddagger}_{cat} - \Delta G^{\ddagger}_{u} = \delta G_{ts} - \delta G_{ip} \\ &= -RT\ln\left(\frac{k_{ip}}{k_i}\right) = -RT\ln\left(\frac{K'_{ip}}{K_{ip}}\right) \qquad (8)\end{aligned}$$

Reaction mechanism, substituent effect

Until recently, nucleophilic substitution reactions on carbonyl carbon atoms were presumed to proceed exclusively by the addition–elimination mechanism *via* a tetrahedral intermediate. It was subsequently found that in a number of cases the splitting of a bond and the formation of a new bond can be simultaneous (concerted, one-step mechanism).[25] A transition from a two-step, addition–elimination mechanism to a one-step, concerted mechanism is realized when the tetrahedral intermediate becomes so unstable that there is no significant barrier to its decomposition (it does not exist for a period of several vibrations) and so it becomes an activated complex.[25]

For instance, in reactions of negatively charged oxygen nucleophiles with substituted phenyl acetates in aqueous solution, the presumed intermediate has too short a lifetime to exist for a significant period, and the reaction takes the concerted pathway.[26] If the leaving oxyanion has a pK_a above *ca* 11, the intermediate is stable enough and the reaction proceeds via the adition–elimination mechanism.[27,28]

The stability of the intermediate also depends on the structure of the acyl group, e.g. replacement of MeCO by MeOCO decreases the stability of the intermediate considerably, so that in some cases the addition–elimination mechanism changes to the concerted mechanism.[29–32] The concerted mechanism is preferred when the polarity of the medium (expressed by quantitative values of solvatochromic parameters, e.g. π^* and α or E_{TN}) decreases.[33]

One of the ways of determining a reaction mechanism consists in the quantitative evaluation of substituent effects (LFER). In an addition–elimination mechanism, the β_{lg} values (obtained from the dependence of log k on pK_a of the conjugated acid of the leaving group[34]) range from 0.1 to 0.3 if the formation of the intermediate is rate-limiting and from 0.8 to 1.3 if the decomposition of the intermediate into products is rate-limiting. For concerted mechanisms these values vary in the range 0.4–0.6,[26,35–37] exceptionally reaching up to about 0.8.[27]

The log k_{i} and log k_{ip} values of splitting off anions of substituted benzamidoximes were correlated with the pK_a values of their conjugated acids measured in methanol. The slope values $\beta_{\text{lg}} = 1.05$ (found in the correlation of k_{i}, i.e. those found in the presence of crown ether) and $\beta_{\text{lg}} = 0.94$ (found in the correlation of k_{ip}) indicate that the reaction takes the addition–elimination mechanism and the rate-limiting step is splitting off of anions of substituted benzamidoximes (see Scheme 4 for the reaction in the presence of crown ether).

The values of β_{lg} for k_{i} and k_{ip} are almost identical, in accordance with the findings[38] concerning alkali metal ion catalysis in nucleophilic displacement reactions of phosphorus-, sulphur- and carbon-based esters by lithium and potassium ethoxides in ethanol, where the rate constant values of reaction with the ion pair are almost the same with lithium ethoxide as with ethoxide ion alone, being *ca* 10% lower with potassium ethoxide than with ethoxide alone; in our case the situation is similar. On the basis of this finding, Pregel *et al.*[38] came to an important conclusion, viz. that the alkali metal ions do not significantly change the activated complex structure.

The situation is different with substituted methyl benzamidoximecarbonates,[3] where $\beta_{\text{lg}} = 0.85$ for the reaction with methoxide ion but 0.53 for that with the ion pair, i.e. a value lower by almost 40%. This relatively large difference in β_{lg} values indicates a considerably different structure of the activated complex and supports the idea of a change in the reaction mechanism from addition–elimination in the presence of the crown ether to concerted in the reaction with the ion pair. Replacement of a phenyl group (substituted *O*-benzoylbenzamidoximes) by a methoxy group (methyl benzamidoximecarbonates) caused such a decrease in the lifetime of the tetrahedral intermediate that it did not exist for a period of several vibrations, and the mechanism changed from addition–elimination to concerted. The splitting off of the benzamidoxime anion from the tetrahedral intermediate in the rate-limiting step is surprising as both the nucleophile (MeO^-) and the leaving group are oxygen anions, and the pK_a of methanol (18.31) is about 1.5–2 times higher than those of substituted benzamidoximes (Table 1). On the other hand, the nucleophilicity of benzamidoxime anions as nucleophiles with an α effect is substantially higher than that of normal oxygen nucleophiles with similar pK_a values.[39] Also, the delocalization of the electron pair on oxygen to the carbonyl group, which would favour the reversible splitting off of the methoxy group in the intermediate, is supported by repulsion from the electron pair of the adjacent nitrogen atom,[3,40] which is further strengthened by the partial charge at the nitrogen atom due to delocalization of electrons from the NH_2 group.

The evaluation of substituent effects in *O*-benzoylbezamidoximes **1a–g** is more complex. The reaction involves both bond formation and bond splitting at carbonyl carbon atoms, and the reaction product, substituted methylbenzoate, has a zero charge like the starting substrate, hence the change of charge at the carbonyl carbon is greater in the activated complex than in the product. The structure of the activated complex approaches that of a tetrahedral intermediate, the hybridization at the carbonyl carbon atom with the strongly polar $C{=}O$ bond being partially changed (from sp^2 to sp^3). This change is considerably affected by substituents in the benzene ring. The addition of water to substituted benzaldehydes, which produces the corresponding neutral diol, exhibits[41] a constant of the equilibrium reaction ρ_{eq} equal to 1.71, although two neutral molecules form a neutral product! The addition of OH to substituted benzaldehydes giving the anion of the corresponding diol exhibits[42] $\rho_{eq} = 2.76$, which means that the ρ value of dissociation of the diol (1.05) is similar to that of substituted benzoic acids. The ρ value found for the reaction with methoxide ion is 2.17 and that for the reaction with the ion pair is 1.98, i.e. again lower by about 10%. This lowering is, as in the previous examples, obviously predominantly due to the presence of metal cation in the activated compex.

An assessment of the extent to which the activated complex of a particular reaction approaches the tetrahedral intermediate was made by comparing the ρ constant of the reaction of 4-nitrophenyl esters of substituted benzoic acids with OH ions going by concerted mechanism (the most recent value found[45] in 10% aqueous acetonitrile is $\rho = 2.14$) with the ρ constant of addition of OH^- ion to substituted benzaldehydes ($\rho_{eq} = 2.76$). From these values, it was concluded[43] that the activated complex structure is close to the intermediate structure.

Comparison of this value with our $\rho = 2.17$ allows the conclusion that in our case also the activated complex structure is close to that of the intermediate, and that the bond splitting between the carbonyl carbon atom and the benzamidoxime oxygen has hardly advanced. This is apparently in contradiction with the high value of $\beta_{lg} = 1.05$ found. In substituted phenyl acetates,[43,44] the oxygen atom of the phenoxy group bears an 'effective charge' of 0.7. In substituted *O*-benzoylamidoximes, the effective charge at the oxygen atom of substituted benzamidoximes is probably still higher because the negative charge transfer to the carbonyl oxygen atom is supported by repulsion from the electron pair of the adjacent nitrogen atom bearing a partial negative charge. By forming the tetrahedral intermediate, this effective charge at oxygen is cancelled, and β_{lg} has a large negative value even if the CO bond splitting has hardly advanced.

Acknowledgements

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