

KINETICS OF METHANOLYSIS OF SUBSTITUTED BENZAMIDE *O*-(PHENOXYCARBONYL)- AND *O*-(ALKOXYCARBONYL)OXIMES CATALYZED BY SODIUM METHANOLATE

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Received May 4, 1998

Accepted September 3, 1998

Dedicated to the memory of Dr Miroslav Protiva.

The kinetics of methanolysis of substituted benzamide *O*-(phenoxy carbonyl)- and *O*-(alkoxy carbonyl)oximes catalyzed by sodium methanolate was studied at 25 °C. The reaction proceeds in two steps. In the first, faster step, the substituted phenoxy group is exchanged for a methoxy group giving rise to substituted *O*-(methoxy carbonyl)oximes. In the second step, a benzamide oxime is eliminated and dimethyl carbonate is formed. The slope of the plot of the rate constant in dependence on the sodium methanolate concentration has an increasing tendency in both steps. In the presence of 18-crown-6, the plots are linear and the rate constants are lower than in the absence of the crown ether. The rate constants of the reaction of the substrate with the methanolate ion and with the MeONa ion pair were determined assuming that the sodium cation-catalyzed reactions constitute the rate-determining step of the reaction of the substrate with the MeONa ion pair. For the elimination of the aryloxy group and of the substituted benzamide oxime, the rate constants of the reaction with the ion pair are roughly twelvefold and twentyfold higher, respectively, than in the uncatalyzed reaction. The slope of the dependence of $\log k$ on the pK_a of the substituted phenols (β_{lg}) has the value of -0.52 for the uncatalyzed reaction of elimination of the substituted phenoxy group, -0.83 for the elimination of the benzamide oxime group, and -0.53 for the reaction with the ion pair. In the first step and probably also in the second step, the reaction proceeds by the concerted mechanism. The relatively high ρ value of methanolysis of substituted benzamide *O*-(4-nitrophenoxy carbonyl)oximes, 0.63, suggests that the structure of the transition state approaches that of the tetrahedral intermediate.

Key words: Benzamide oxime carbonates; Catalysis with sodium ion; Methanolysis kinetics; Dissociation constants; Concerted mechanism.

During our investigation of the base-catalyzed cyclization of amide oxime carbonates to 1,2,4-oxadiazole derivatives^{1,2} we found that in methanolic

solutions of sodium methanolate, only methanolysis occurs, rather than the expected cyclization reaction. Therefore we decided to study in detail the base-catalyzed methanolysis of substituted benzamide *O*-(phenoxy-carbonyl)- and *O*-(alkoxycarbonyl)oximes to identify the reaction mechanism and elucidate and evaluate the effect of the sodium methanolate concentration.

EXPERIMENTAL

Temperature data have not been corrected. ^1H NMR spectra of deuteriochloroform solutions at 25 °C were measured on a Bruker AMX 360 instrument at 360.14 MHz. Chemical shifts are relative to the signals of the non-deuterated solvent ($\delta(^1\text{H})$ 7.25 CHCl_3).

Electronic spectra were scanned on a Hewlett-Packard 8453 Diode Array Spectrophotometer at 25 °C. The reaction products and intermediates were identified by liquid chromatography-mass spectrometry using a Waters 616 chromatograph coupled with a VG-Platform FISON-ESP-3000D mass spectrometer, and by gas chromatography using a MEGA 5160 instrument.

Chemicals

The substituted benzamide oximes were synthesized from hydroxylamine and substituted benzonitriles as described in refs^{2,3}. The benzamide *O*-(phenoxy-carbonyl)- and *O*-(alkoxy-carbonyl)oximes **1a–1s** and **2a–2i** were prepared from the benzamide oximes and chloroformates (Scheme 1) by the general procedures *A* (compounds **1**) and *B* (compounds **2**). Characteristic data of the carbonates are given in Tables I and II.

Procedure A. Substituted benzamide oxime (10 mmol) is dissolved in dichloromethane (25 ml), and triethylamine (1.43 ml, 10 mmol) is added. A aryl chloroformate (10 ml) in dichloromethane (50 ml) is added within 15 min to the stirred and cooled (0 °C) solution, and the reaction mixture is stirred at 0–10 °C for another 20 min, until the crude product separates. The latter is filtered off, washed with water and ether, and recrystallized from ethanol.

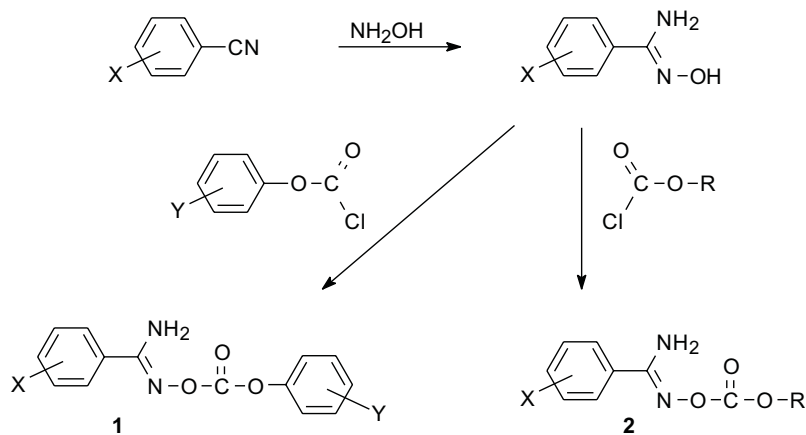
Procedure B. The components are mixed as in procedure *A*. After addition of alkyl chloroformate, the mixture is refluxed for 10–15 min, cooled to room temperature, and shaken with 100 ml of water. The organic phase is separated and dried, and the solvent is evaporated. The distillation residue is recrystallized from aqueous ethanol and washed with ether.

Benzaldehyde *O*-(4-nitrophenoxy-carbonyl)oxime (**3**) was prepared from benzaldoxime and 4-nitrophenyl chloroformate in ether in the presence of pyridine; yield 89%. Melting temperature 134–136 °C (chloroform) agrees with the published data⁴.

Dissociation Constants

The dissociation constants of the substituted benzamide oximes were determined spectrophotometrically in methanolic solutions: 2 ml of a methanolic solution of sodium methanolate, $c = 0.005\text{--}3 \text{ mol l}^{-1}$, was pipetted into a quartz cell with a stopper placed in the thermostatted unit of the spectrophotometer at 25 °C, 20 μl of a methanolic solution of

substrate ($c = 0.01 \text{ mol l}^{-1}$) was injected into the solution by means of a Hamilton syringe, the cell contents were stirred, and the spectrum (200–500 nm) was measured within 5 s. The absorbances of the anion (A_B) and of the neutral species (A_{BH}) were measured in solutions containing sodium methanolate and acetate buffer in concentrations of 3.0 and 1.0 mol l^{-1} , respectively. The $\text{p}K_a$ values were calculated using Eq. (1) (ref.⁵):



1	X	Y	2	X	R
a	4-OMe	4-NO ₂	a	4-OMe	Me
b	4-Me	4-NO ₂	b	4-Me	Me
c	H	4-NO ₂	c	H	Me
d	4-Cl	4-NO ₂	d	4-Cl	Me
e	3-Cl	4-NO ₂	e	3-Cl	Me
f	3-NO ₂	4-NO ₂	f	3-NO ₂	Me
g	4-NO ₂	4-NO ₂	g	4-NO ₂	Me
h	4-OMe	H	h	H	Et
i	4-Me	H	i	H	iPr
j	H	H			
k	4-Cl	H			
l	3-Cl	H			
m	3-NO ₂	H			
n	4-NO ₂	H			
o	H	4-Cl			
p	H	3-Cl			
r	H	3-NO ₂			
s	4-NO ₂	3-Cl			

SCHEME 1

TABLE I
Melting points, yields and elemental analysis data for benzamide *O*-(phenoxy-carbonyl)- and *O*-(alkoxy-carbonyl)oximes **1a-1s** and **2a-2i**

Compound	M.p., °C	Yield, %	Formula M.w.	Calculated/Found			
				% C	% H	% N	% Cl
1a	111.5–113	73	C ₁₃ H ₁₃ N ₃ O ₆	54.38	3.96	12.68	–
			331.3	54.62	4.00	12.56	
1b	125–126.5	76	C ₁₃ H ₁₃ N ₃ O ₅	57.15	4.16	13.33	–
			315.3	56.99	4.19	13.35	
1c	118–120	63	C ₁₄ H ₁₁ N ₃ O ₅	55.82	3.68	13.95	–
			301.3	56.03	3.74	13.86	
1d	128–130	39	C ₁₄ H ₁₀ ClN ₃ O ₆	50.09	3.00	12.52	10.56
			335.7	49.83	3.02	12.25	10.38
1e	121–123	44	C ₁₄ H ₁₀ ClN ₃ O ₆	50.09	3.00	12.52	10.56
			335.7	50.01	3.12	12.80	10.43
1f	138–140	44	C ₁₄ H ₁₀ N ₄ O ₇	48.56	2.91	16.18	–
			346.3	48.79	3.04	16.17	
1g	119–121	35	C ₁₄ H ₁₀ N ₄ O ₇	48.56	2.91	16.18	–
			346.5	48.37	3.08	16.15	
1h	129–130	66	C ₁₃ H ₁₄ N ₂ O ₄	62.93	4.93	9.79	–
			286.3	62.82	4.89	9.72	
1i	128–129	56	C ₁₃ H ₁₄ N ₂ O ₃	6.66	5.22	10.36	–
			270.3	66.64	5.21	10.30	
1j	125–127	53	C ₁₄ H ₁₂ N ₂ O ₃	65.62	4.72	10.93	–
			256.3	65.70	4.87	10.90	
1k	156–157	49	C ₁₄ H ₁₁ ClN ₂ O ₃	57.84	3.81	9.64	12.20
			290.7	58.10	3.81	9.58	12.29
1l	108–110	41	C ₁₄ H ₁₁ ClN ₂ O ₃	57.84	3.81	9.64	12.20
			290.7	57.72	3.94	9.81	11.94
1m	129–131	58	C ₁₄ H ₁₁ N ₃ O ₅	55.82	3.68	13.95	–
			301.3	55.96	3.83	14.17	
1n	157–160	32	C ₁₄ H ₁₁ N ₃ O ₅	55.82	3.68	13.95	–
			301.3	55.73	3.55	13.81	

TABLE I
(Continued)

Compound	M.p., °C	Yield, %	Formula M.w.	Calculated/Found			
				% C	% H	% N	% Cl
1o	130–132	83	C ₁₄ H ₁₁ ClN ₂ O ₃	57.84	3.81	9.64	12.20
			290.7	57.64	3.75	9.80	12.37
1p	115–117	74	C ₁₄ H ₁₁ ClN ₂ O ₃	57.84	3.81	9.64	12.20
			290.7	57.71	3.86	9.93	12.10
1r	116–118	77	C ₁₄ H ₁₁ N ₃ O ₅	55.82	3.68	13.95	–
			301.3	55.73	3.46	13.72	–
1s	155–158	32	C ₁₄ H ₁₀ ClN ₃ O ₅	50.09	3.00	12.52	10.56
			335.7	49.92	3.05	12.39	10.72
2a	115–117	81	C ₁₀ H ₁₂ N ₂ O ₄	53.55	5.40	12.50	–
			224.2	53.70	5.22	12.76	–
2b	112–115	82	C ₁₀ H ₁₂ N ₂ O ₃	57.67	5.81	13.46	–
			208.2	57.61	5.88	13.52	–
2c	128–131	83	C ₉ H ₁₀ N ₂ O ₃	55.67	5.19	14.43	–
			194.2	55.55	5.15	14.27	–
2d	151–153	36	C ₉ H ₉ ClN ₂ O ₃	47.36	3.98	12.28	15.51
			228.6	47.50	3.91	12.42	15.38
2e	97–99	47	C ₉ H ₉ ClN ₂ O ₃	47.28	3.97	12.25	15.51
			228.6	47.19	3.93	12.27	15.44
2f	169–171	64	C ₉ H ₉ N ₃ O ₅	45.19	3.79	17.57	–
			239.2	45.21	3.92	17.69	–
2g	197–200	17	C ₉ H ₉ N ₃ O ₅	45.18	3.79	17.57	–
			239.2	45.03	3.84	17.63	–
2h	125–127	57	C ₁₀ H ₁₂ N ₂ O ₃	57.67	5.81	13.46	–
			208.2	57.87	5.83	13.52	–
2i	103–104	24	C ₁₁ H ₁₄ N ₂ O ₃	59.43	6.35	12.61	–
			222.2	59.36	6.39	12.66	–

TABLE II
 ^1H NMR spectra of benzamide *O*-(phenoxy carbonyl)- and *O*-(alkoxy carbonyl)oximes **1a-1s** and **2a-2i** in CDCl_3

Compound	δ , ppm; J , Hz
1a	3.84 s, 3 H (OCH_3); 5.18 brs, 2 H (NH_2); 6.94 d, 2 H, $^3J = 8.6$ (H-2, H-4); 7.44 d, 2 H, $^3J = 9.0$ (H-6, H-10); 7.65 d, 2 H (H-1, H-5); 8.29 d, 2 H (H-7, H-9)
1b	2.38 s, 3 H (CH_3); 5.20 brs, 2 H (NH_2); 7.22–7.25 m, 2 H (H-2, H-4); 7.42–7.45 m, 2 H (H-6, H-10); 7.57–7.60 m, 2 H (H-1, H-5); 8.27–8.30 m, 2 H (H-7, H-9)
1c	3.44 brs, 2 H (NH_2); 7.50–7.58 m, 3 H (H-2, H-3, H-4); 7.66–7.68 d, 2 H, $^3J = 9.1$ (H-6, H-10); 7.76–7.78 d, 2 H, $^3J = 7.9$ (H-1, H-5); 8.38–8.40 d, 2 H (H-7, H-9)
1d	5.18 brs, 2 H (NH_2); 7.41–7.45 m, 4 H (H-2, H-4, H-6, H-10); 7.64–7.67 m, 2 H (H-1, H-5); 8.28–8.31 m, 2 H (H-7, H-9)
1e	5.21 brs, 2 H (NH_2); 7.36–7.48 m, 4 H (H-1, H-3, H-5); 7.54–7.60 d, 2 H, $^3J = 5.9$ (H-6, H-10); 7.71–7.72 d, 1 H, $^3J = 1.3$ (H-5); 8.29–8.31 d, $^3J = 7.1$ (H-7, H-9);
1f	5.32 brs, 2 H (NH_2); 7.44–7.48 m, 2 H (H-6, H-10); 7.64–7.69 t, 1 H, $^3J = 7.9$ (H-2); 8.10–8.13 m, 1 H (H-1); 8.29–8.33 m, 2 H (H-7, H-9); 8.36–8.39 m, 1 H (H-3); 8.55–8.56 t, 1 H, $^3J = 1.8$ (H-5)
1g	5.30 brs, 2 H (NH_2); 7.44–7.47 m, 2 H (H-1, H-5); 7.91–7.94 m, 2 H (H-6, H-10); 8.29–8.32 m, 4 H (H-2, H-4, H-7, H-9)
1h	3.83 s, 3 H (OCH_3); 5.10 brs, 2 H (NH_2); 6.91–6.93 m, 2 H (H-2, H-4); 7.22–7.26 m, 3 H (H-7, H-8, H-9); 7.37–7.41 m, 2 H (H-6, H-10); 7.64–7.66 m, 2 H (H-1, H-5)
1i	2.38 s, 3 H (CH_3); 5.12 brs, 2 H (NH_2); 7.21–7.25 m, 5 H (H-2, H-4, H-7, H-8, H-9); 7.37–7.41 m, 2 H (H-6, H-10); 7.59–7.61 m, 2 H (H-1, H-5)
1j	5.11 brs, 2 H (NH_2); 7.33–7.35 m, 3 H (H-6, H-8, H-10); 7.51–7.53 m, 5 H (H-2, H-4, H-7, H-9); 7.74–7.77 m, 2 H (H-1, H-5)
1k	5.14 brs, 2 H (NH_2); 7.21–7.25 m, 5 H (H-6, H-7, H-9, H-10); 7.38–7.41 m, 2 H (H-1, H-5); 7.64–7.67 m, 2 H (H-2, H-4)
1l	brs, 2 H (NH_2); 7.21–7.25 m, 2 H (H-6, H-9); 7.33–7.42 m, 4 H (H-2, H-8, H-7, H-9); 7.44–7.47 m, 1 H (H-3); 7.70–7.71 t, 1 H, $^4J = 1.8$ (H-5)
1m	5.33 brs, 2 H (NH_2); 7.23–7.29 m, 3 H (H-7, H-8, H-9); 7.38–7.43 m, 2 H (H-6, H-10); 7.60–7.65 t, 1 H, $^3J = 8.0$ (H-2); 8.09–8.12 m, 1 H (H-1); 8.32–8.36 m, 1 H (H-3); 8.53–8.54 t, 1 H, $^4J = 1.9$ (H-5)
1n	2.26 brs, 2 H (NH_2); 7.22–7.27 m, 3 H (H-7, H-8, H-9); 7.39–7.43 m, 2 H (H-6, H-10); 7.90–7.92 m, 2 H (H-1, H-5); 8.27–8.30 m, 2 H (H-2, H-4)
1o	5.18 brs, 2 H (NH_2); 7.14–7.20 m, 2 H (H-6, H-10); 7.34–7.36 m, 2 H (H-7, H-9); 7.44–7.47 m, 2 H (H-2, H-4); 7.47–7.49 m, 1 H (H-3); 7.69–7.70 m, 2 H (H-1, H-5)
1p	5.18 brs, 2 H (NH_2); 7.15–7.17 m, 1 H (H-10); 7.23–7.27 m, 2 H (H-6, H-8); 7.30–7.35 t, 1 H, $^3J = 8.0$ (H-9); 7.41–7.45 m, 2 H (H-2, H-4); 7.48–7.52 m, 1 H (H-3); 7.69–7.71 d, 2 H, $^3J = 7.2$ (H-1)

TABLE II
(Continued)

Compound	δ , ppm; J , Hz
1r	5.23 brs, 2 H (NH ₂); 7.42–7.46 t, 2 H, ³ J = 7.5 (H-2); 7.49–7.53 t, 1 H, ³ J = 7.3 (H-3); 7.61–7.66 m, 2 H (H-9, H-10); 7.70–7.72 d, 2 H, ³ J = 7.3 (H-1, H-5); 8.13–8.21 m, 2 H (H-6, H-8)
1s	2.26, 5.27 brs, 2 H (NH ₂); 7.16–7.18 m, 1 H (H-10); 7.25–7.28 m, 2 H (H-6, H-8); 7.32–7.37 t, 1 H, ³ J = 8.0 (H-9); 7.91–7.93 m, 2 H (H-1, H-5); 8.29–8.31 m, 2 H (H-2, H-4)
2a	3.81 s, 3 H (Ph-OCH ₃); 3.88 s, 3 H (OCH ₃); 5.02 brs, 2 H (NH ₂); 6.88–9.91 m, 2 H (H-2, H-4); 7.58–7.62 m, 2 H (H-1, H-5)
2b	2.37 s, 3 H (CH ₃); 3.88 s, 3 H (OCH ₃); 5.07 brs, 2 H (NH ₂); 7.19–7.21 m, 2 H (H-2, H-4); 7.54–7.57 m, 2 H (H-1, H-5)
2c	3.87 s, 3 H (OCH ₃); 5.16 brs, 2 H (NH ₂); 7.37–7.40 m, 2 H (H-2, H-4); 7.44–7.46 m, 1 H (H-3); 7.64–7.66 m, 2 H (H-1, H-5)
2d	3.89 s, 3 H (OCH ₃); 5.08 brs 2 H (NH ₂); 7.37–7.39 m, 2 H (H-1, H-5); 7.60–7.63 m, 2 H (H-2, H-4)
2e	3.89 s, 3 H (OCH ₃); 5.14 brs, 2 H (NH ₂); 7.32–7.36 t, 1 H, ³ J = 6.1 (H-2); 7.42–7.45 m, 1 H (H-1); 7.54–7.57 m, 1 H (H-3); 7.67–7.68 t, 1 H, ⁴ J = 1.8 (H-4)
2f	3.91 s, 3 H (OCH ₃); 5.19 brs, 2 H (NH ₂); 7.60–7.65 t, 1 H, ³ J = 6.2 (H-2); 8.07–8.10 m, 1 H (H-1); 8.32–8.36 m, 1 H (H-3); 8.52–8.53 t, 1 H, ⁴ J = 1.9 (H-4)
2g	3.84 s, 3 H (OCH ₃); 7.17 brs, 2 H (NH ₂); 8.00–8.02 m, 2 H (H-1, H-5); 8.36–8.34 m, 2 H (H-2, H-4)
2h	1.31 t, 3 H, J = 7.1 (CH ₃); 4.24 k, 2 H, J = 4.2 (O-CH ₂); 6.86 brs, 2 H (NH ₂); 7.46–7.49 m, 2 H (H-2, H-4); 7.52–7.54 m, 2 H (H-3); 7.71–7.74 m, 2 H (H-1, H-5)
2i	1.31 d, 6 H, J = 4.1 (2 \text{ } \backslash \text{ } \text{CH}_3); 4.90 m, J = 6.2 (OCH); 6.84 brs, 2 H (NH ₂); 7.47–7.49 m, 2 H (H-2, H-4); 7.51–7.54 m, 2 H (H-3); 7.71–7.74 m, 2 H (H-1, H-5)

$$pK_a = \log [\text{MeO}^-] + pK_s - \log ((A - A_{\text{BH}})/(A_{\text{B}} - A)) , \quad (I)$$

where A is absorbance of the solution measured and $pK_s = 16.92$.

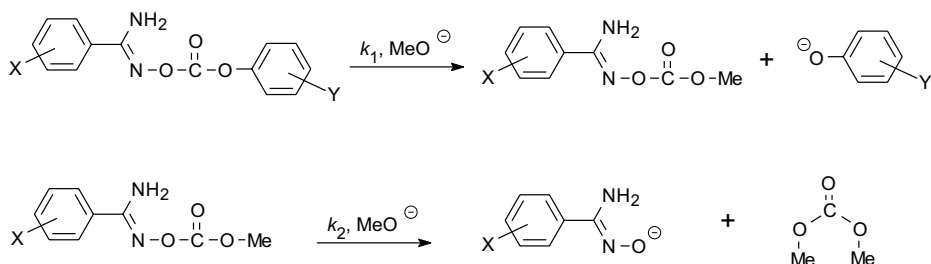
Kinetic Measurements

Two ml of a methanolic solution of sodium methanolate, $c = 0.005\text{--}0.14 \text{ mol l}^{-1}$, was pipetted into a 1-cm quartz cell with a stopper placed in the spectrophotometer block thermostatted at 25 °C. In experiments involving 18-crown-6, the concentration of the latter

invariably exceeded that of sodium methanolate by 0.002 mol l^{-1} . A volume of 10–20 μl of a methanolic solution of substrate, $c = 0.01 \text{ mol l}^{-1}$, was injected into the system, the whole was stirred, and the change in absorbance was recorded. In experiments where the half-life of elimination of the aryloxy group was below 5 s, the kinetic measurements were performed by the stopped-flow method on a Durrum D-150 instrument.

RESULTS

The methanolysis of the substituted benzamide *O*-(phoxycarbonyl)- and *O*-(alkoxycarbonyl)oximes **1a–1s** and **2a–2i** proceeds in two steps: in the first step, the phenoxy group is substituted by a methoxy group, and in the second step, benzamide oxime is eliminated and dimethyl carbonate forms (Scheme 2).



SCHEME 2

The reaction kinetics was examined using excess sodium methanolate, owing to which the methanolysis proceeded as a pseudo-first-order reaction. Where substituent Y was a 3- or 4-nitro group, the first reaction step was considerably faster than the second step, and both reactions could be kinetically investigated separately. For the remaining derivatives, the rate constants were determined on the basis of Eq. (2) (ref.⁶):

$$\text{Abs}_\infty - \text{Abs}_t = \text{Ae}^{-k_1 t} + \text{Be}^{-k_2 t} \quad (2)$$

The second-step rate constants measured for the specifically prepared benzamide *O*-(phoxycarbonyl)- and *O*-(alkoxycarbonyl)oximes **2a–2g** were all consistent with those based on the kinetics of consecutive reactions (Table III).

The slopes of the rate constant dependences on sodium methanolate concentration all exhibited an increasing tendency (Figs 1a, 1b), although in

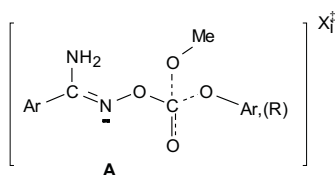
TABLE III

Rate constants k_{ip} , k_p , and k_{C18} ($l \text{ mol}^{-1} \text{ s}^{-1}$) for methanolysis of 4-nitrophenyl carbonates **1a-1g** and methyl carbonates **2a-2g** (Scheme 2) in sodium methanolate solutions at 25 °C in the presence and in the absence of 18-crown-6. The values in parentheses were obtained by evaluation of the consecutive reaction of substances **1a-1g**

Compound ^a	k_{11} ^b	k_{11C18}	k_{ip1} ^b	Compound ^c	k_{12} ^b	k_{12C18}	k_{ip2} ^b
1a	25.73 ± 0.99	24.58 ± 0.87	324.1 ± 14.48	2a	0.17 ± 0.01 (0.19 ± 0.02)	0.20 ± 0.01 (0.18 ± 0.01)	4.66 ± 0.29 (4.72 ± 0.33)
1b	31.31 ± 2.12	32.61 ± 0.52	359.2 ± 30.94	2b	0.22 ± 0.02 (0.24 ± 0.01)	0.25 ± 0.01 (0.23 ± 0.02)	5.39 ± 0.19 (5.45 ± 0.27)
1c	44.60 ± 2.82	40.51 ± 1.40	566.2 ± 41.14	2c	0.29 ± 0.05 (0.32 ± 0.02)	0.31 ± 0.01 (0.29 ± 0.01)	5.96 ± 0.51 (6.07 ± 0.9)
1d	45.94 ± 1.64	47.27 ± 1.39	894.6 ± 24.00	2d	0.38 ± 0.04 (0.41 ± 0.02)	0.42 ± 0.00 (0.40 ± 0.02)	7.77 ± 0.47 (7.82 ± 0.38)
1e	69.06 ± 4.68	78.24 ± 0.99	915 ± 68.33	2e	0.57 ± 0.03 (0.55 ± 0.02)	0.53 ± 0.01 (0.56 ± 0.01)	9.06 ± 0.32 (9.34 ± 0.67)
1f	92.20 ± 1.71	92.36 ± 3.35	1 209 ± 25.2	2f	0.76 ± 0.02 (0.77 ± 0.03)	0.78 ± 0.02 (0.77 ± 0.01)	10.12 ± 0.25 (10.21 ± 0.38)
1g	111.80 ± 9.0	133.93 ± 1.9	1 731 ± 132.1	2g	0.86 ± 0.04 (0.84 ± 0.03)	0.81 ± 0.02 (0.87 ± 0.04)	11.49 ± 0.50 (12.03 ± 0.61)

^a λ_{anal} 400 nm; ^b calculated by using Eq. (5); ^c λ_{anal} 280 nm.

the transition state of the assumed structure **A**, the second molecule of the methoxide ion could not play any role. The explanation of the increasing



slope which is based on the change in the ionic strength is not likely either because the sodium ion concentration never exceeded 0.15 mol l^{-1} and the transition state during the reaction of the substrate with the methanolate ion has the same charge as the starting reactants. The most likely explanation consists in a catalytic effect of the sodium ions. Therefore, the measurements were repeated with a small excess of 18-crown-6. The k_{obs} vs methanolate concentration plot was linear in such cases (Figs 1a, 1b) and the k_{obs} values were always lower than the corresponding values found in the absence of the crown ether. This implies that the sodium ion catalyzes the methanolysis of the substrate.

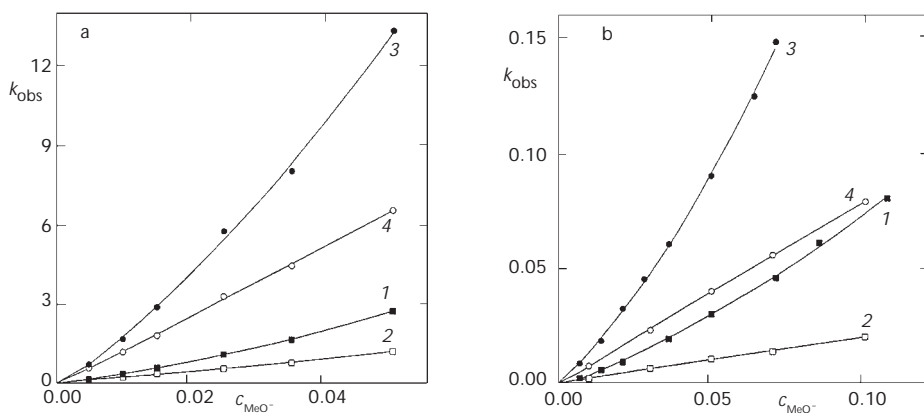


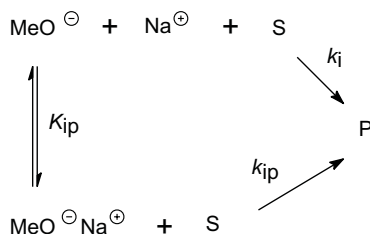
FIG. 1

Dependence of k_{obs} (s^{-1}) on methanolate concentration (mol l^{-1}) for methanolysis of benzamide *O*-(phenoxy carbonyl)oximes **1a** (1, 2) and **1g** (3, 4) in the absence (full symbols) and presence (open symbols) of 18-crown-6, for the first (a) and second (b) steps of methanolysis

DISCUSSION

Catalytic Effect of Sodium Ions

Association of oppositely charged ions giving rise to ion pairs occurs in alcoholic solutions of alcoholates and alkali metal ions. Until recently it was mostly assumed that ion pairs are less reactive than free ions⁷. In fact, this rule is strictly valid for S_N2 reactions. On the other hand, in nucleophilic addition reactions proceeding at the carbonyl carbon atom, ion pairs frequently exhibit enhanced reactivity^{8,9}. The increasing slope of the dependence of k_{obs} on sodium methanolate concentration is then explained by parallel reactions of the substrate with the anion and with the ion pair which is more reactive than the anion itself (Scheme 3).



SCHEME 3

The k_i and k_{ip} values are rate constants for the reaction of the substrate with the anion and the ion pair, respectively, and K_{ip} (Eq. (3)) is the equilibrium constant of association of the anion with the cation; its value is 7.5 (ref.¹⁰).

$$K_{\text{ip}} = \frac{[\text{MeONa}]}{[\text{MeO}^-][\text{Na}^+](\gamma_{\pm})^2} = \frac{[\text{MeONa}]}{[\text{MeO}^-]^2(\gamma_{\pm})^2} \quad (3)$$

While the activity coefficient of the ion pair is assumed to be unity, *i.e.*, the activity of the ion pair is identical with its concentration, the activity coefficients of the sodium and methoxide ions are described by Eq. (4) (ref.¹¹):

$$-\log \gamma_{\pm} = \frac{1.69 \sqrt{I}}{1 + 2.5 \sqrt{I}} \quad (4)$$

The observed rate constant in the absence of crown ether is given by Eq. (5):

$$k_{\text{obs}} = k_i [\text{MeO}^-] + k_{\text{ip}} [\text{MeONa}] = k_i [\text{MeO}^-] + k_{\text{ip}} K_{\text{ip}} [\text{MeO}^-]^2 (\gamma_{\pm})^2 \quad (5)$$

The actual concentration of the methoxide ion was calculated using Eq. (6):

$$[\text{MeO}^-] = \frac{-1 \pm \sqrt{1 + 4c_{\text{MeO}^-} K_{\text{ip}} (\gamma_{\pm})^2}}{2K_{\text{ip}} (\gamma_{\pm})^2} \quad (6)$$

The dependence of $k_{\text{obs}}/[\text{MeO}^-]$ on $K_{\text{ip}}[\text{MeO}^-](\gamma_{\pm})^2$ is linear, its slope and intercept being k_{ip} and k_i , respectively (Fig. 2). Table IV gives the k_{obs} , γ^2 , and $[\text{MeO}^-]$ values for the dependence shown in Fig. 2.

The k_{ip} and k_i values found from the transformed equation (5) and the k_{IC18} values for the reaction of the substrate with the anion in the presence of 18-crown-6 are given in Table IV for the 4-nitrophenyl carbonates **1a-1g** and methyl carbonates **2a-2g**. Table V gives the k_i values for substances **1h-1s**.

Although an appreciable effect of the ion pair on the reaction rate was observed for the methanolysis of all of the substrates measured by us, catalysis by the ion pair was not found for the methanolysis of phenyl acetate¹² or ethanolysis of 4-nitrophenyl benzoate¹³, where $k_{\text{ip}} = 102$ (ref.¹³). On the other hand, a substantial acceleration by the sodium ion has been found in the methanolysis of 2-acetoxyphenyl 3,6,9,12-tetraoxatridecyl ether¹² (**4**) and ethanolysis of 3- and 4-nitrophenyl 2-furoate¹⁴ (**5**).

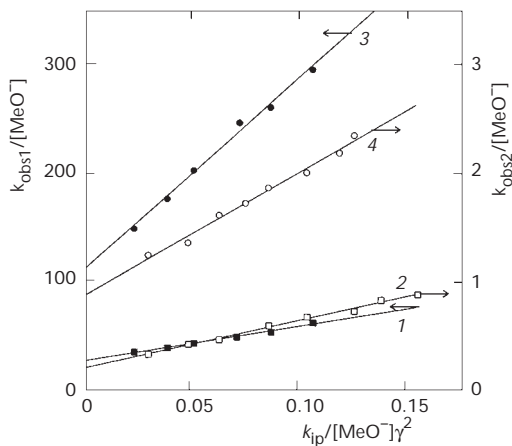
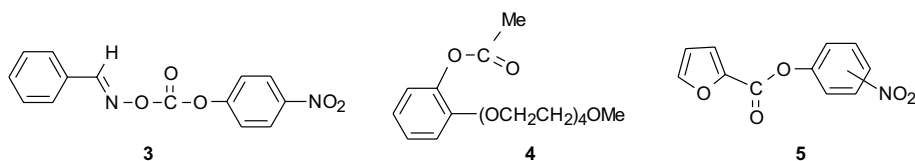


FIG. 2
Dependence of $k_{\text{obs}}/[\text{MeO}^-]$ on $k_{\text{ip}}[\text{MeO}^-](\gamma_{\pm})^2$ for the first (full symbols) and second (open symbols) reaction steps of methanolysis of benzamide *O*-(phenoxy-carbonyl)oximes **1a** (1, 2) and **1g** (3, 4); the slope and intercept give k_{ip} and k_i , respectively

In both cases, the formation of a complex (chelate) of the sodium ion with the ether and carbonyl oxygen atoms in the starting as well as transition state is conceivable. The reason why the reaction of the methanolate ion with benzamide oxime carbonates is catalyzed by sodium ions may rest



in the presence of the NH_2 group which enhances the stability of the transition state complex with the sodium ion. To test this hypothesis, we measured the kinetics of the second step of the reaction of compound **3** with the methoxide ion both in the presence and in the absence of the crown ether. In both cases was the dependence of k_{obs} on the methanolate concen-

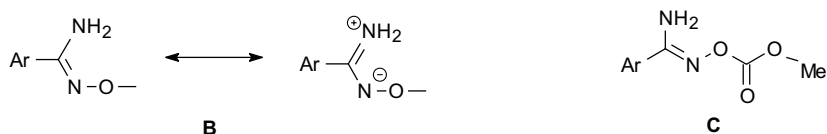
TABLE IV

Values of k_{obs} (s^{-1}), γ^2 , and $[\text{MeO}^-]$ for the first (k_{obs1}) and second (k_{obs2}) step of methanolysis of benzamide *O*-(phenoxy carbonyl)oximes **1a** and **1g**

$c_{\text{MeO}^-} \cdot 10^{-2}$ mol l^{-1}	$[\text{MeO}^-] \cdot 10^{-2}$ mol l^{-1}	$(\gamma_{\pm})^2$	1a		1g	
			k_{obs1}	$k_{\text{obs2}} \cdot 10^2$	k_{obs1}	$k_{\text{obs2}} \cdot 10^2$
0.5	0.49	0.62	0.17	–	0.72	–
0.7	0.69	0.57	–	0.22	–	0.85
1.0	0.96	0.53	0.37	–	1.69	–
1.5	1.43	0.47	0.60	0.57	2.89	1.84
2.5	2.34	0.40	1.12	0.92	5.78	4.54
3.5	3.22	0.36	1.69	1.91	8.06	6.09
5.0	4.51	0.31	2.77	2.99	13.33	9.03
6.4	5.72	0.28	–	–	–	12.49
7.1	6.31	0.26	–	4.60	–	14.81
8.5	7.49	0.24	–	6.15	–	–
10.7	9.23	0.22	–	8.08	–	–
14.2	12.06	0.20	–	10.85	–	–

tration linear and the k_{obs} values for the same methanolate concentrations were virtually identical, *viz.* $k_i = 5.57 \pm 0.23 \text{ l mol}^{-1} \text{ s}^{-1}$ and $k_{\text{IC18}} = 5.51 \pm 0.17 \text{ l mol}^{-1} \text{ s}^{-1}$, respectively.

Although the formation of a complex of the sodium ion with the carbonyl oxygen and amino group nitrogen is conceivable, we do not consider it likely because the electron pair of the amino group is partly delocalized (resonance structure **B**) so that the complex formation would be associated with an appreciable loss of delocalization energy.



It is more probable that the sodium ion is complexed with the carbonyl group oxygen and with the electron pair of the partly negatively charged double-bonded nitrogen atom. In addition, the non-complexed substrate **C** possesses the *Z*-configuration at the C=N bond and the antiperiplanar conformation about the N-O bond¹⁵.

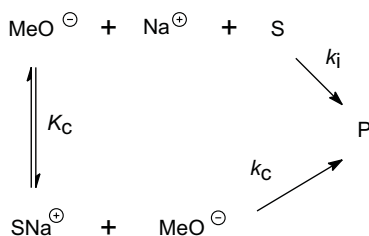
Ercolani and Mandolini¹² assumed that during the methanolysis of the ether **4**, the methanolate ion reacts with the complex of the ether with the sodium ion (Scheme 4), and they calculated the equilibrium constant for the complexation with the sodium ion, $K_c = 175 \text{ l mol}^{-1}$.

TABLE V

Rate constants k_{IC18} ($\text{l mol}^{-1} \text{ s}^{-1}$) for the first step of methanolysis of compounds **1h-1s** (Scheme 2) at 25 °C in sodium methanolate solutions containing 18-crown-6; λ_{anal} 285 nm

Compound	k_{IC18}	Compound	k_{IC18}
1h	0.92 ± 0.04	1n	6.90 ± 0.22
1i	1.45 ± 0.04	1o	5.87 ± 0.13
1j	2.00 ± 0.05	1p	7.48 ± 0.30
1k	2.18 ± 0.05	1r	22.47 ± 0.65
1l	2.71 ± 0.06	1s^a	44.51 ± 1.48
1m	3.89 ± 0.08		

^a λ_{anal} 240 nm.



SCHEME 4

Assuming that for low sodium methanolate concentrations the activity coefficient of the complex of substrate with the sodium ion, SNa^+ , equals that of the sodium ion, the K_c value can be expressed by Eq. (7):

$$K_c = \frac{[\text{SNa}]^{\ddagger} \gamma^{\ddagger}}{[\text{S}][\text{Na}^+] \gamma^{\ddagger}} = \frac{[\text{SNa}]^{\ddagger}}{[\text{S}][\text{Na}^+]}. \quad (7)$$

The rate of the reaction proceeding *via* the SNa^+ complex is given by Eq. (8):

$$\begin{aligned}
 v_c &= k_c [\text{SNa}^+] [\text{MeO}^-] (\gamma^{\ddagger})^2 = k_c K_c [\text{S}][\text{Na}^+] [\text{MeO}^-] (\gamma^{\ddagger})^2 = \\
 &= k_c K_c [\text{S}] [\text{MeO}^-]^2 (\gamma^{\ddagger})^2,
 \end{aligned} \quad (8)$$

the sodium ion concentration being again equal to that of the methanolate because the sodium ion proportion complexed with the substrate is negligibly low in comparison with the total sodium ion concentration.

In this case, the actual concentration $[\text{S}]$ decreases with the concentration of $[\text{Na}^+]$ due to the formation of the $[\text{SNa}^+]$ complex. Using Eq. (6) and substituting $(c_s - [\text{S}])$ for $[\text{SNa}^+]$, the dependence of $[\text{S}]$ on $[\text{MeO}^-]$ is

$$[\text{S}] = \frac{c_s}{K_c [\text{MeO}^-] + 1}, \quad (9)$$

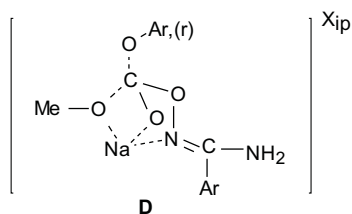
so that

$$k_{\text{obs}} = \frac{v}{c_s} = \frac{1}{K_c [\text{MeO}^-] + 1} \left[k_i [\text{MeO}^-] + (K_{\text{ip}} k_{\text{ip}} + K_c k_c) [\text{MeO}^-]^2 (\gamma^{\ddagger})^2 \right]. \quad (10)$$

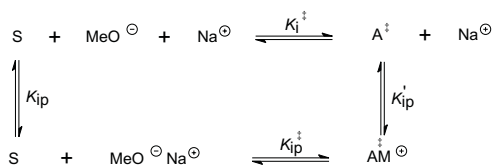
This means that the sodium ion-catalyzed reaction can proceed *via* the ion pair and/or *via* the substrate complex with the sodium ion. The kinetic pro-

cedures are unable to discriminate between the pathways because both obey the same rate equation¹⁶. The sodium ion can form a complex with the substrate; at the same time, however, the reaction of the substrate with the ion pair may be the major reaction pathway, catalyzed by the sodium ion.

At sufficiently high K_c values at higher methanolate concentrations, the $k_{\text{obs}}/[\text{MeO}^-]$ vs $[\text{MeO}^-]$ plots exhibit an inflection because $[\text{SNa}^+]$ no more increases linearly with $[\text{MeO}^-]$. We calculated this dependence theoretically for Eq. (10) assuming that the reaction proceeds *via* the $[\text{SNa}^+]$ complex and the K_c value is identical with the K_{ip} value (7.5 l mol^{-1} , Fig. 3, dashed line). This dependence is entirely different from that calculated assuming that the K_c value is negligible and the catalyzed reaction proceeds *via* the ion pair (Eq. (5), Fig. 3, full line). Therefore, we suggest that the kinetically decisive pathway is *via* the ion pair, as defined by the initial rate equation (5). In the transition state, the sodium cation interacts simultaneously with the methanolate ion and carbonyl group oxygen atoms and with the double-bonded nitrogen atom (structure **D**).



In terms of transition state theory, the kinetic data can be separated into the contribution of stabilization by the sodium ion to the initial state and the transition state. The degree of stabilization of the transition state can be evaluated by the method developed by Kurz¹⁷ and by Dunn and Buncel¹⁸ (Scheme 5). K_i^\ddagger and K_{ip}^\ddagger are the equilibrium constants of the uncatalyzed and catalyzed formation of the transition states A^\ddagger and $A^\ddagger\text{M}^+$, respectively,



SCHEME 5

and K'_{ip} is the association constant of complexation of the sodium ion with the transition state A^\ddagger of the uncatalyzed reaction. This virtual association constant can be calculated based on the thermodynamic cycle.

Since – according to activated complex theory – the transition state concentrations are in equilibrium with the reactant concentrations and, at the same time, the two starting ions are in equilibrium with the ion pair, the two activated complexes are in equilibrium as well, although no actual direct dynamic equilibrium exists between them¹⁷.

The rate constants are given by Eq. (11):

$$k = \frac{kT}{h} e^{-\Delta G^\ddagger/RT} = \frac{kT}{h} K^\ddagger, \quad (11)$$

and so K'_{ip} can be calculated as

$$K'_{ip} = \frac{k_{ip} K_{ip}}{k_i}. \quad (12)$$

The change in the Gibbs energy of the ion pair formation δG_{ip} is calculated from Eq. (13):

$$-\delta G_{ip} = RT \ln K_{ip}. \quad (13)$$

FIG. 3
The dependence of observed values of k_{obs1} and k_{obs2} (s^{-1}) on methanolate concentration ($mol\ l^{-1}$) for the first (1) and second (2) reaction steps of methanolysis of benzamide *O*-(phenoxy-carbonyl)-oxime **1g**, theoretical plots for the two steps calculated on the basis of Eq. (5) (—), and theoretical plot for the 2nd step calculated on the basis of Eq. (10) assuming that the reaction proceeds via the $[SNa^+]$ complex and that $K_c = K_{ip} = 7.5\ l\ mol^{-1}$

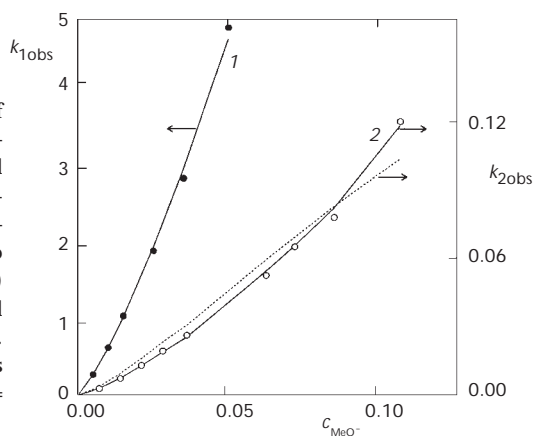


Figure 4 shows the relative changes in the Gibbs energies (kJ mol^{-1}) for the sodium ion-catalyzed (cat) and uncatalyzed (u) first step of methanolysis of substance **1g** relative to the zero energy level of the starting substances.

Catalysis takes place if the metal cation stabilizes more the activated complex than the ground state, whereas inhibition takes place if the reverse is true. The resulting catalytic effect ΔG_{cat} is described by Eq. (14):

$$\Delta G_{\text{cat}} = \Delta G_{\text{cat}}^{\ddagger} - \Delta G_{\text{u}}^{\ddagger} = \delta G_{\text{is}}^{\text{ts}} - \delta G_{\text{ip}} = -RT \ln \left(\frac{k_{\text{ip}}}{k_{\text{i}}} \right) = -RT \ln \left(\frac{K'_{\text{ip}}}{K_{\text{ip}}} \right). \quad (14)$$

Reaction Mechanism, Substituent Effect

It was assumed until recently that nucleophilic substitution reactions at the carbonyl carbon atom proceed exclusively by the addition-elimination mechanism *via* a tetrahedral intermediate. Only in the past 20–30 years it was found that in several cases, bond formation and splitting can occur simultaneously by a concerted one-step mechanism¹⁹. The two-step addition-elimination mechanism is replaced by the one-step concerted mechanism if the tetrahedral intermediate is so unstable that no sufficient significant barrier exists for its decay (it does not exist for several vibrations) and it becomes a transition state²⁰.

For instance, in the reaction of negatively charged nucleophiles with substituted phenyl acetates in aqueous solutions, the presumed intermediate

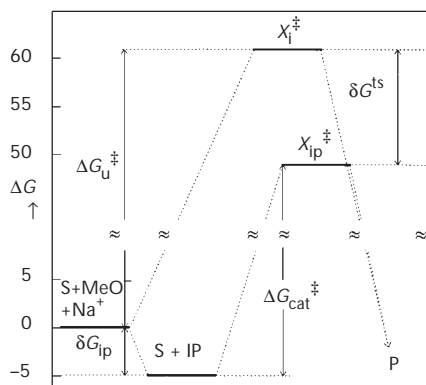


FIG. 4
Relative changes in the Gibbs energies (kJ mol^{-1}) of the species shown for the first step of methanolysis of benzamide *O*-(phenoxy carbonyl)oxime **1g** relative to the zero energy level of the starting compounds

possesses too short a lifetime to be capable of existence and the reaction proceeds by the concerted mechanism²¹. If the pK_a of the leaving oxy anion is higher than approximately 11, the intermediate is sufficiently stable and the reaction proceeds by the addition-elimination mechanism^{21,22}.

The stability of the intermediate also depends on the structure of the acyl group: for instance, replacement of $CH_3-C=O$ by $CH_3O-C=O$ reduces appreciably the stability of the intermediate, owing to which the addition-elimination mechanism is replaced by the concerted mechanism in some cases²³⁻²⁶. The latter mechanism is preferred if the polarity of medium (in terms of solvatochromic parameters²⁷ such as π^* and α or E_T^N) decreases²⁸.

Among ways of elucidating the reaction mechanism is the quantitative evaluation of the substituent effects (LFER). For the addition-elimination mechanism, the β_{lg} values (found on the basis of the $\log k$ vs pK_a dependence for the conjugate acid of the leaving group²⁹) lie within the range of 0.1–0.3 if the formation of the intermediate is the rate-determining process, and 0.8–1.0 or up to 1.3 if the decomposition of the intermediate to the products is the rate-determining process. For the concerted mechanism, the values lie typically^{20,30-32} within the range of 0.4–0.6 and rarely attain values²¹ as high as 0.8.

The $\log k_i$ values for the elimination of substituted phenolate ions and the $\log k_i$ and $\log k_{ip}$ values of substituted benzamide oxime anions have been correlated with the pK_a values of their acids³³ (see below) measured in the same medium, and with the σ constants³⁴.

The $\log k_i$ values for the elimination of phenoxy groups correlate with the σ constants also in the case of the 4- NO_2 group, whereas in the correlation with pK_a , this group constitutes an outlier. This is due to the imbalance between the change in the charge at the phenoxy group oxygen in the transition state and the degree of delocalization of the π electrons because delocalization of π electrons lags behind the charge transfer in the transition state and does not occur to a sufficient extent until the C–O bond is broken to a large part^{20,35-37}.

The value of $\beta_{lg} = -0.52$ for the elimination of phenolate ions (except for the 4-nitro derivative) is consistent with the fact that the reaction proceeds by the concerted mechanism. In comparison with the reaction of substituted phenyl acetates, the stabilization of the hypothetical intermediate is additionally reduced by the replacement of the methyl group by the amide oxime group and by the replacement of the environment by a less polar one.

The situation is more intricate for the reaction of substances **2a–2g** with the methanolate ion, where $\beta_{lg} = -0.85$, which rather suggests the two-step mechanism, with the decomposition of the intermediate as the rate-determining step. The methoxy group and methanol should reduce the stability of the intermediate if any, whereas the high pK_a value of the substituted benzamide oximes (see Table VI) should increase it.

However, it is impossible to determine which of the effects predominate. The pK_a values of benzamide oximes are about two orders of magnitude lower than the pK_a value of methanol, which is 18.31 (ref.³⁸); on the other hand, the nucleophilicity of benzamide oxime anions as nucleophiles with the α effect is substantially higher than it is usual with normal oxygen-containing nucleophiles possessing the same pK_a (ref.³⁹). Also, delocalization of the electron pair from the oxygen to the carbonyl group, which would make the reversible elimination of the methoxy group during the formation of the intermediate more favourable, is promoted by the electron repulsion from the neighbouring nitrogen atom possessing a fractional negative charge⁴⁰.

The β_{lg} value for the methanolysis catalyzed by the sodium ion is considerably lower than for the uncatalyzed reaction, *viz.* 0.53 vs 0.85, and is typical of reactions proceeding by the concerted mechanism. It is likely that the uncatalyzed reaction proceeds by that mechanism as well. The lower β_{lg} value for the catalyzed reaction may be due to the fact that in the leaving anions of the substituted benzamide oximes, the double-bonded nitrogen atom is complexed with the sodium cation, so that during the reaction the substituent "can see" a smaller change in the negative charge only. It is not impossible, though, that in the uncatalyzed reaction, the elimination of benzamide oxime from the tetrahedral intermediate is the rate-determining

TABLE VI
Values of pK_a of the substituted benzamide oximes in methanol at 25 °C

X	pK_a , 25 °C	X	pK_a , 25 °C
4-OMe	16.83 ± 0.03	3-Cl	16.39 ± 0.03
4-Me	16.73 ± 0.01	3-NO ₂	16.19 ± 0.02
H	16.67 ± 0.02	4-NO ₂	16.10 ± 0.02
4-Cl	16.48 ± 0.03		

step and the reaction mechanism is different if catalysis by the sodium cation is used.

Evaluation of the effect of substitution for the benzamide *O*-(phenoxy-carbonyl)oximes **1a–1g** is a more complicated task. The bond at the carbonyl carbon is also cleaved during the reaction, and the reaction product possesses a zero charge, as does the starting substrate, so that the change in the charge at the carbonyl carbon is higher for the transition state than for the product³². The structure of the transition state approaches that of the tetrahedral intermediate, and a partial change in hybridization (from sp^2 to sp^3) of the carbonyl carbon with the strongly polar C=O bond takes place⁴¹. This conversion is affected appreciably by the benzene ring substituents. For the addition of water to substituted benzaldehydes, giving rise to the neutral diol, the ρ_{eq} is 1.71 (ref.⁴²) although a neutral product forms from two neutral molecules. For the addition of OH^- to substituted benzaldehydes giving rise to the diol anion, the ρ_{eq} value is 2.76 (ref.⁴³), which implies that the ρ value for the dissociation of the diol, 1.05, is similar to that for substituted benzoic acids.

An assessment of the extent to which the transition state of a reaction approaches the tetrahedral intermediate has been made by comparing the ρ constants for the reaction of 4-nitrophenyl esters of substituted benzoic acids, which proceeds by the concerted mechanism with OH^- ions (the most recent value for solutions in 10% aqueous acetonitrile is 2.14 (ref.⁴¹), and the ρ constant of hydroxyl ion addition to substituted benzaldehydes⁴⁴. From this comparison, the author inferred that the structure of the transition state approaches that of the intermediate.

In the methanolysis of benzamide *O*-(phenoxy-carbonyl)oximes **1a–1g**, the fact should be taken into account that the observed ρ value, 0.63, is reduced considerably due to the occurrence of three additional atoms between the reaction centre and substituent ($-C(NH_2)=N-O-$); their effect on the ρ value, *i.e.* their transmission factor, should be determined³⁴. The effect of the $-C(NH_2)=N-$ group can be ascertained based on the ρ constant ratio for the dissociation of diols (1.05) and benzaldoxime (0.66). Assuming that the replacement of water by methanol as a solvent brings about increase in the ρ constant by *ca* 20%, the resulting transmission factor value is $0.63/1.25 \approx 0.5$.

The next atom, oxygen, reduces the transmission factor twofold³⁴, approximately to 0.25. Multiplying the ρ constant for the hydrolysis of 4-nitrophenyl benzoates, 2.14, by this transmission factor, we obtain a value of 0.54, which – in view of the approximations used – is not substantially different from the value observed for methanolysis, 0.56. Hence, it

can be concluded that in this case, also, the structure of the transition state approaches that of the tetrahedral intermediate.

This work was supported by the Grant Agency of the Czech Republic (grant No. 203/97/0545).

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