Base-catalysed hydrolysis and reactivity-spectra correlations of (*Z*)-4-benzylidene-2-(substituted phenyl)oxazol-5(4*H*)-ones†

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Rate coefficients have been measured for the base-catalysed hydrolysis of a series of (*Z*)-4-benzylidene-2-(substituted phenyl)-4*H*-oxazol-5-ones in 70% v/v aqueous dioxan at various temperatures. The enthalpies and entropies of activation, and a Hammett reaction constant for the reaction, have been evaluated. The ^{1}H and ^{13}C NMR chemical shifts were assigned, as well as the IR carbonyl stretching frequencies in chloroform, after deconvolution and band separation. Successful correlations between the carbonyl stretching wavenumbers and the ^{13}C NMR chemical shifts and the rates of the alkaline hydrolysis were found.

Keywords: oxazolones, base-catalysed hydrolysis, Fermi resonance, NMR, polar substituent effects

Introduction

The (*Z*)-4-benzylidene-2-(substituted phenyl)oxazol-5(4*H*)-ones (**1**) shown in Scheme 1 are an interesting series of unsaturated five-membered ring lactones. 2-Phenyloxazol-5(4*H*)-ones are significant intermediates in chiral aminoacid synthesis. Aminoacids are prepared by hydrolysis or alcoholysis of the endocyclic carboxyl group in the oxazolone ring.[1,2]

Reactivity and spectral correlations with structure of (*Z*)-4-(substituted benzylidene)-2-phenyloxazol-5(4*H*)-ones have been studied previously.[3] These lactones are much more reactive than the comparable acyclic esters or relatively large ring lactones. Study of the alkaline hydrolysis of (*Z*)-4-benzylidene-2-phenyloxazol-5(4*H*)-one revealed that the electronegative nitrogen atom in the ring provides an activating effect.[3]

The aim of the present work is to investigate the base-catalysed hydrolysis of (*Z*)-4-benzylidene-2-(substituted phenyl)oxazol-5(4*H*)-ones in 70% v/v aqueous dioxan at various temperatures. The obtained rate constants are related to the substituent effects in terms of Hammett constants, the carbonyl stretching frequencies, as well as to ^{13}C chemical shifts of endocyclic carbons in the oxazolone ring.

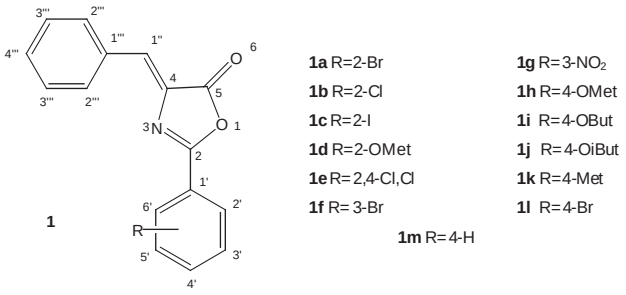
Results

Alkaline hydrolysis

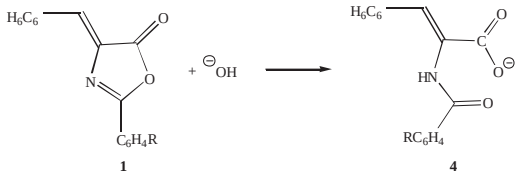
The rate coefficients for the alkaline hydrolysis of (*Z*)-4-benzylidene-2-(substituted phenyl)oxazol-5(4*H*)-ones (**1**) in 70% v/v aqueous dioxan at various temperatures are listed in Table 1. The corresponding activation parameters are given in Table 2. The reaction was found to be first order both in substrate and in hydroxide ion (see Figs 1 and 2).

Alkaline hydrolysis of (*Z*)-4-benzylidene-2-(substituted phenyl)oxazol-5(4*H*)-ones (**1**) leads to ring opening according to Scheme 2. The corresponding ions of 2-benzamido-3-arylpropenoic acid[4] are the reaction products, as confirmed previously.[3]

The reaction pathway shown in Scheme 3 involves the addition of hydroxide ion to the oxazolone carbonyl group to form the tetrahedral intermediate **2**, followed by ring fission to give the anion **3**. The rate-determining step is considered to be k_1, as found for the series of unsaturated lactones studied previously.[3-6]



Scheme 1



Scheme 2

Table 1 Rate coefficients[a] (*k*) for the alkaline hydrolysis of (*Z*)-4-benzylidene-2-(substituted phenyl)oxazol-5(4*H*)-ones in 70% (v/v) aqueous dioxan

Compound (substituent)	*k* / dm^3 mol^{-1} s^{-1}			
	295.1 K	304.4 K	310.4 K	318.7 K
1a (2-Br)	13.2	25.8	39.1	67.7
1b (2-Cl)	14.6	26.4	37.9	61.3
1c (2-I)	12.7	23.2	33.6	54.9
1d (2-OMe)	7.41	11.8	15.6	22.7
1e (2,4-Cl$_2$)	29.6	45.3	58.7	82.9
1f (3-Br)	17.8	33.5	49.6	82.9
1g (3-NO$_2$)	41.8	76.6	111	182
1h (4-OMe)	6.90	13.7	20.8	36.1
1i (4-OBu)	8.16	13.7	18.9	28.9
1j (4-OiBu)	6.96	11.4	15.4	23.0
1k (4-Me)	8.99	14.0	18.4	26.3
1l (4-Br)	14.5	28.6	43.4	75.3
1m (H)	13.2[b]	24.5[b]	35.8[b]	59.4[b]

[a]Rate coefficients were reproducible to ±4%. Wavelength used to monitor hydrolysis was 375 nm.
[b]Taken from ref. 3.

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† This work is dedicated to Associate Professor Dr. Alexander Perjéssy (1941–2003), *in memoriam*.

Table 2 Activation parameters[a] for the alkaline hydrolysis of (*Z*)-4-benzylidene-2-(substituted phenyl)oxazol-5(4*H*)-ones in 70% (v/v) aqueous dioxan

Subst.	E_A (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	Subst.	E_A (kJ mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})
2-Br	54.2	51.6	–83	4-OMe	54.9	52.3	–86
2-Cl	47.5	45.0	–105	4-OBu	41.9	39.4	–128
2-I	48.6	46.1	–102	4-OiBu	39.6	37.0	–138
2-OMe	36.9	34.4	–146	4-Me	35.4	32.9	–151
2,4-Cl_2	34.1	31.7	–144	4-Br	54.6	52.0	–81
3-Br	51.0	48.4	–91	4-H		46[b]	–66[b]
3-NO_2	48.6	46.1	–90				

[a]E_A and $\Delta H^{\neq}$ were reproducible to ±1.5 kJ mol^{-1}, $\Delta S^{\neq}$ to ±5 J K^{-1} mol^{-1}.
[b]Taken from ref. 3.

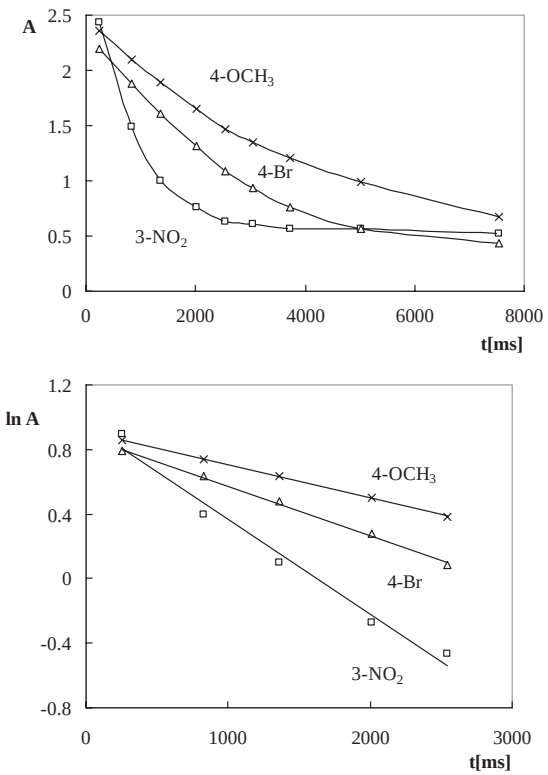


Fig. 1 Plots of absorbance at 375 nm *vs* time for alkaline hydrolysis of (Z)-4-benzylidene-2-(3-nitrophenyl)oxazol-5(4H)-one (□), (*Z*)-4-benzylidene-2-(4-bromphenyl)-oxazol-5(4*H*)-one (Δ) and (*Z*)-4-benzylidene-2-(4-methoxyphenyl)oxazol-5(4*H*)-one (x) in 70% aqueous dioxan at 304,4 K [OH^-]=1.58×10^{-2} mol dm^{-3}.

IR, UV-VIS and NMR spectroscopy

The IR absorption bands of the C=O stretching vibrations of compounds **1** in the region of 1870–1710 cm^{-1} in $CHCl_3$ exhibit clear splitting. It has been found on the basis of similar behaviour of (*Z*)-4-(substituted benzylidene)-2-phenyloxazol-5(4*H*)-ones[3] and other unsaturated lactones[7] that this splitting is caused by two-level Fermi resonance interaction between the C=O stretching mode and the first overtone of an out-of-plane deformation vibration of C–H group. In order to obtain unperturbed wavenumbers for both fundamental (C=O) and the first overtone ω_{02}(C–H) absorption bands, the relations based on the method Langseth and Lord and improved by Nyquist *et al.*[8] have been applied. The band in the doublet associated with the branch A belongs after elimination of resonance to the fundamental ν(C=O) stretching vibration.[3]

The results of mathematical deconvolution and band separation are listed in Table 3. The very intense band in the region of 1710–1620 cm^{-1} was assigned, by analogy with the previously studied[3] (*Z*)-4-(substituted benzylidene)-2-phenyloxazol-5(4*H*)-ones, to the fundamental C=N stretching vibration of the oxazolone ring.

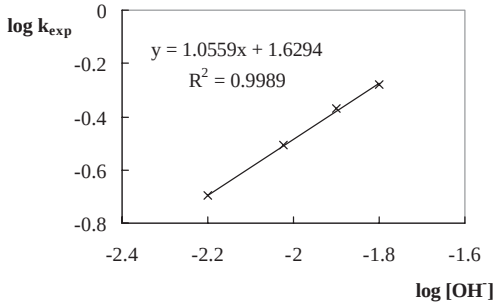
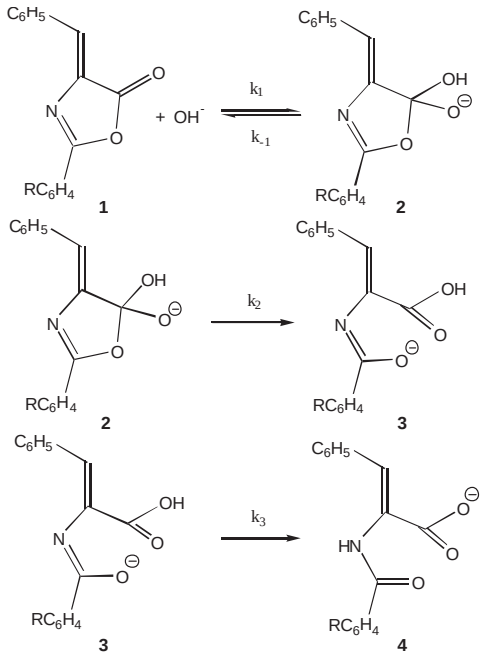


Fig. 2 Plot of observed rate constant vs. concentration of hydroxide ions at 304.4 K for alkaline hydrolysis of (*Z*)-4-benzylidene-2-(4-methoxyphenyl)oxazol-5(4*H*)-one at 318.2 K.

UV-VIS study of (*Z*)-4-benzylidene-2-(substituted phenyl)oxazol-5(4*H*)-ones (**1**) in 70% (v/v) aqueous dioxan revealed in the region of 300–420 nm a broad and strong absorption band (log ε ≈ 4) with discernible vibrational splitting. Wavelengths in the maximum of the peak are given in Table 4. This band probably belongs to π–π* transition. Its intensity was used when monitoring alkaline hydrolysis of compounds **1** because other components of the reaction mixture did not absorb in this region (Fig. 3).

^{1}H and ^{13}C NMR chemical shifts for (*Z*)-4-benzylidene-2-(substituted phenyl)oxazol-5(4*H*)-ones in $CDCl_3$ are given in Tables 5 and 6. Individual chemical shifts were assigned using ^{1}H–^{13}C correlation techniques[9] and have not been previously reported.



Scheme 3

Table 3 Wave numbers (in cm^{-1}) of the C=O stretching vibration and the first overtone of the C–H out-of-plane deformation vibration for (*Z*)-4-benzylidene-2-(substituted phenyl)oxazol-5(4*H*)-ones in $CHCl_3$. Integrated intensities are given in $dm^3\ mol^{-1}\ cm^2$

Subst.	Perturbed data[a]				Unperturbed data[b]		
	Branch A		Branch B				
	ν_A	I_A	ν_B	I_B	ν(C=O)	ω_{02}(CH)	W_{AB}
2-Br	1792.6	5.40	1766.2	0.85	1789.0	1769.8	9.06
2-Cl	1793.3	5.33	1767.4	1.09	1788.9	1771.8	9.72
2-I	1792.2	5.06	1766.0	0.82	1788.5	1769.7	9.08
2-OMe	1791.0	4.47	1771.9	2.38	1784.4	1778.5	9.10
2,4-Cl_2	1795.5	5.37	1768.2	1.24	1790.4	1773.3	10.66
3-Br	1799.0	4.65	1772.7	1.71	1791.9	1779.8	11.66
3-NO_2	1810.7	2.79	1787.1	3.45	1797.6	1800.2	11.73
4-OMe	1791.6	5.14	1764.8	1.14	1786.8	1769.7	10.32
4-OBu	1791.2	5.15	1765.0	1.14	1786.5	1769.7	10.09
4-OiBu	1791.0	5.49	1764.7	0.87	1787.4	1768.3	9.04
4-Me	1792.1	4.97	1765.7	1.08	1787.4	1770.4	10.12
4-Br	1794.6	5.09	1768.4	1.00	1790.3	1772.7	9.71

[a]After deconvolution and band separation.
[b]Corrected for Fermi resonance.

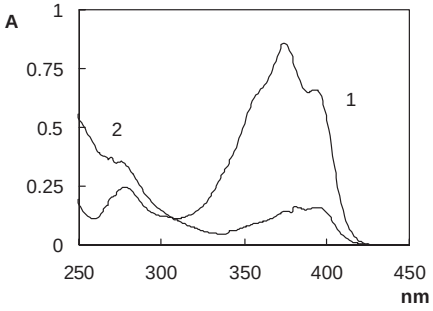


Fig. 3 UV-VIS spectrum of (*Z*)-4-benzylidene-2-(4-isobutoxyphenyl)oxazol-5(4*H*)-one (**1j**) and the spectrum of reaction product (**2**) in 70% (v/v) aqueous dioxane.

Table 4 Wavenumbers (in cm^{-1}) of the C=N stretching vibration and of the C–H out-of-plane deformation vibration in $CHCl_3$ together with wavelengths (in nm) of peak maximum in 70% aqueous dioxane for (*Z*)-4-benzylidene-2-(substituted phenyl)oxazol-5(4*H*)-ones

Subst.	ω_{01}(CH)	ν(C=N)	λ_{max}
2-Br	886.4	1654.0	364
2-Cl	886.4	1654.0	364
2-I	886.4	1652.0	367
2-OMe	878.4	1652.4	372
2,4-Cl_2	872.4	1654.4	368
3-Br	892.4	1654.0	365
3-NO_2	873.6	1655.6	366
4-OMe	886.4	1654.0	374
4-OBu	886.4	1653.6	375
4-OiBu	886.4	1653.6	374
4-Me	886.4	1654.8	367
4-Br	888.0	1654.4	369

Table 5 ^1H chemical shifts (in ppm) for (*Z*)-4-benzylidene-2-(substituted phenyl)oxazol-5(4*H*)-ones in $CDCl_3$

Subst.	2′	3′	4′	5′	6′	1″	2‴	3‴, 4‴
2-Br	–	7.64	7.32	7.27	7.90	7.15	8.08	7.32
2-Cl	–	7.40	7.47	7.33	8.01	7.21	8.14	7.40
2-I	–	7.97	7.43	7.15	8.10	7.21	8.25	7.43
2-OMe	–	7.01	7.48	7.01	8.01	7.16	8.15	7.40
2.4-Cl_2	–	7.64	–	7.45	8.08	7.37	8.24	7.51
3-Br	8.33	–	7.75	7.43	8.10	7.29	8.20	7.52
3-NO_2	9.02	–	8.48	7.77	8.09	7.37	8.22	7.53
4-OMe	8.16	7.05	–	7.05	8.16	7.27	8.22	7.49
4-OBu	8.20	7.05	–	7.05	8.20	7.21	8.23	7.45
4-OiBu	8.05	6.94	–	6.94	8.05	7.10	8.12	7.40
4-Me	8.15	7.41	–	7.41	8.15	7.29	8.28	7.55
4-Br	8.09	7.73	–	7.73	8.09	7.33	8.24	7.54

Discussion

Configuration and conformation

Each of the compounds **1** may exist in one of two configurations *E* or *Z* with respect to the exocyclic C=C double bond. In addition for 2- and 3- substituted derivatives each of these two configurations gives rise to two conformations due to rotation around C_2–$C_{1'}$ axis. The four possible isomeric configurational and conformational structures are shown in Scheme 4.

According to the results of AM1 calculations, listed in Table 7, for all studied compounds the **Z** configuration is predicted to be the most stable. This is in complete agreement with IR spectroscopic observations for compounds **1** because Fermi resonance interaction requires spatial proximity of vibrating groups, *i.e.* C=O and C-H groups.[10] The Z configuration has been reported for many similar unsaturated lactones studied previously.[3-6]

3- and 4-substituted phenyl system

The Hammett equation[11] (1) given in Eqn (1):

$$\log k = \rho\sigma + \log k_0 \qquad (1)$$

can be applied directly only to the 3- and 4-substituted phenyl-lactones in which the spatial proximity between substituent and reacting carbonyl group can be neglected. The correlations with σ, σ^+ and σ^- constants[12] are given in Table 8. The rate constant for (*Z*)-4-benzylidene-2-phenyloxazol-5(4*H*)-one is taken from ref. 3. The substituents 4-butoxy and 4-isobutoxy are omitted from correlations because their σ values have not been found. Correlation between rate coefficients and σ values is illustrated in Fig. 4.

The reaction constant, ρ, is 0.74. This value is higher comparing to the σ value for the hydrolysis of (*Z*)-4-(substituted benzylidene)-2-phenyloxazol-5(4*H*)-ones.[3] This observation predicts more effective transmission of polar effects to the reaction site in compounds **1.** This is probably owing to the fact that the aromatic system in the present case is directly bonded to the oxazolone ring.

2-Substituted phenyl systems

Many attempts have been made to correlate the reactivity of 2- substituted phenyl systems.[13] It has been proposed that *para*-σ values be used to correlate *ortho*-substituent effects.[4] These correlations are given in *Table* 8 and include the rate constant for (*Z*)-4-benzylidene-2-phenyloxazol-5(4H)-one taken from ref. 3. The ρ value is 0.58 which is about 78% of the same value reported for the 3-/4- substituted lactones. This indicates a reduction in transmission of the polar effects for the 2- position comparing with 3-/4- position.

Table 6 Selected ^{13}C chemical shifts (in ppm) for (*Z*)-4-benzylidene-2-(substituted phenyl)oxazol-5(4*H*)-ones in $CDCl_3$[a].

Subst.	**2**	**5**	**1´**	**5´**	**6´**	**1´´**	**2´´´**
2-Br	161.46	166.70	122.44	132.05	132.63	133.27	133.25
2-Cl	161.20	166.74	124.00	131.88	131.65	133.05	132.54
2-I	161.93	166.99	128.96	128.99	142.72	133.37	133.22
2-OMe	162.61	167.71	114.44	120.88	131.72	131.37	132.61
2.4-Cl_2	160.33	166.36	122.39	(131.48)	(132.40)	133.41	(132.25)
3-Br	162.05	166.98	123.10	128.99	126.84	132.86	132.62
3-NO_2	161.41	166.67	127.65	(133.63)	(134.25)	132.84	(127.47)
4-OMe	(163.40)	167.88	118.01	114.63	130.54	130.29	132.31
4-OBu	(163.41)	167.85	117.64	115.15	130.65	130.21	132.44
4-OiBu	(163.29)	167.72	117.55	114.97	130.56	130.10	132.37
4-Me	163.56	167.67	122.79	129.72	128.41	131.04	132.37
4-Br	162.75	167.20	124.61	132.41	129.71	132.41	132.57

[a]Values in brackets are of uncertain assignment.

Table 7 Calculated AM1 energies (in kJ mol^{-1})[a] of the various configurations[b] for (*Z*)-4-benzylidene-2-(substituted phenyl) oxazol-5(4*H*)-ones.

Cmpd.	-*E*	Cmpd.	-*E*	Cmpd.	-*E*
1a(Z1)	**3442.108**	**1d**(E1)	3702.411	**1h(Z)**	**3849.296**
1a(Z2)	3433.495	**1d**(E2)	3698.600	**1h**(E)	3705.323
1a(E1)	3298.752	**1e(Z1)**	**3440.797**	**1i(Z)**	**4691.419**
1a(E2)	3297.653	**1e**(Z2)	3435.909	**1i**(E)	4546.418
1b(Z1)	**3459.223**	**1e**(E1)	3297.300	**1j(Z)**	**4689.386**
1b(Z2)	3454.322	**1e**(E2)	3295.362	**1j**(E)	4544.385
1b(E1)	3315.698	**1f**(Z1)	3453.497	**1k(Z)**	**3766.459**
1b(E2)	3313.713	**1f(Z2)**	**3453.578**	**1k**(E)	3655.494
1c(Z1)	**3428.725**	**1f**(E1)	3309.649	**1l(Z)**	**3456.673**
1c(Z2)	3409.660	**1f**(E2)	3309.594	**1l**(E)	3309.792
1c(E1)	3285.416	**1g**(Z1)	3532.958	**1m(Z)**	**3484.882**
1c(E2)	3285.480	**1g(Z2)**	**3533.558**	**1m**(E)	3340.937
1d(Z1)	**3846.080**	**1g**(E1)	3389.430		
1d(Z2)	3843.250	**1g**(E2)	3389.319		

[a]1 a.u. = 27.21 eV = 2 628.1 kJ mol^{-1}.
[b]See Scheme 4.

(*Z*)-4-Benzylidene-(2,4-dichlorophenyl)oxazol-5(*4H*)-one has been excluded from correlations. The ratio k(2,4-Cl_2)/k(2-Cl) = 1.7 (at 304.4 K) predicts that the polar effect of Cl substituent in position 4 is enhanced with the effect from the second substituent in the 2 position.

The rate of alkaline hydrolysis decreases in the order 2-Cl > 2-Br > 2-I > 2-OCH_3. Large substituents caused inhibition of alkaline hydrolysis. This is in agreement with the structure (Z2) from AM1 calculations (Table 7) and predicts that large substituents will interfere with the co-planar geometry of the studied compounds **1**.

Correlation of rates and carbonyl stretching wave numbers

Kinetic coefficients have been successfully correlated with carbonyl stretching frequencies in chloroform using Eqn (2):

$$\log k = a\,\nu_{CO} + \text{constant} \qquad (2)$$

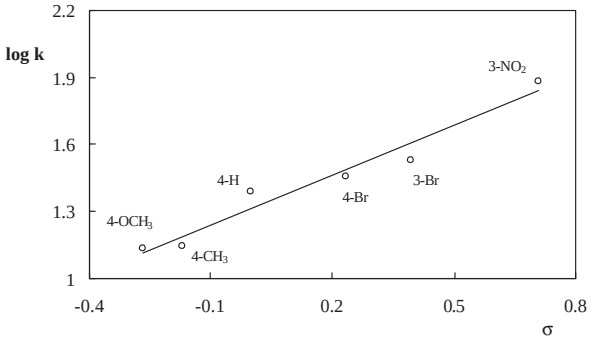
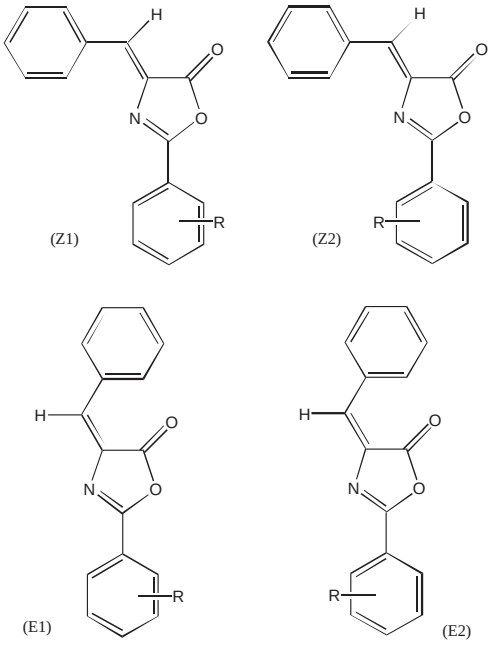


Fig. 4 Dependence of the rate coefficients (at 304.4 K) of alkaline hydrolysis on σ values for (*Z*)-4-benzylidene-2-(substituted phenyl)oxazol-5(4*H*)-ones.



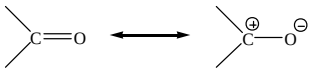
Scheme 4

Table 8 Correlations[a] between rate coefficients, substituent constants[b], IR spectral data and NMR spectral data for (*Z*)-4-benzylidene-2-(substituted phenyl)oxazol-5(4*H*)-ones[c]

3-/4- substituted phenyl system						
y	*x*	*p*	*q*	*r*	*n*	*ex*
log k^d	σ	0.736	1.31	0.978	6	1i. 1j
log k^d	σ^+	0.494	1.41	0.936	6	1i. 1j
log k^d	σ^-	0.807	1.27	0.972	6	1i. 1j
log k^d	ν(C=O)	0.0735	-130.1	0.980	7	13
log k^d	δ($^{13}C_5$)	-0.605	102.6	-0.955	8	-
log k^d	δ($^{13}C_2$)	-0.351	58.50	-0.963	8	-
log k^d	δ($^{13}C_{1''}$)	0.162	-20.0	0.969	7	9
2- substituted phenyl system						
y	*x*	ρ	*q*	*r*	*n*	*ex*
log k^d	σ*	0.577	1.32	0.962	4	12
log k^d	ν(C=O)	0.0751	-133.0	0.979	5	-
All derivatives						
y	*x*	ρ	*q*	*r*	*n*	*ex*
log k^d	ν(C=O)	0.0694	-122.9	0.911	13	-

[a]y = ρx+q.
[b]See ref. 12
[c]n is a number of independent variables. r is the correlation coefficient and ex are the compounds excluded from correlations.
[d]At 304.4 K.

This correlation is remarkable in that it covers such a diverse range of substitution and is independent of the position of the substituent in the phenyl ring (Table 8). It can be concluded that the factors controlling reactivity and carbonyl stretching frequencies must be the same. The stabilisation of the transition state relative to initial state for the alkaline hydrolysis by electrostatic field effects must be duplicated in the stretching vibrations, as indicated previously.[4,5] The latter has been succesfully presented by the competing canonical structures **5** and **6.**



5 **6**

Correlation of rates and ^{13}C chemical shifts

In order to study precisely electrostatic field effects on reactivity, correlations between kinetic coefficients and ^{13}C chemical shifts using equation (3) have been investigated.

$$\log k = b\,\delta(^{13}C) + \text{constant} \qquad (3)$$

Results for carbons C_2, C_5 and $C_{1''}$ are given in Table 8. All correlations are satisfactory. This indicates that charge distribution on carbons inside but also outside of the oxazolone ring effects the reactivity of functional group. Sensitivity of the field effect (indicated by the slope) decreases with the spatial distance of carbon from the reactive functional group.

Experimental

The preparation of (*Z*)-4-benzylidene-2-(substituted phenyl)oxazol-5(4*H*)-ones has been reported previously.[3] Physical properties are given in Table 9. Elemental analyses are in Table 10. The purity of the lactones was monitored by IR and ^1H and ^{13}C NMR spectroscopy.

Kinetic measurements

Standard 0.1 mol dm^{-3} sodium hydroxide was prepared by appropriate dilution with deionised water of carbonate free saturated sodium hydroxide solution. The reaction was followed spectrophotometrically in a termostated cell at the wavelength 375 nm using Aminco-Morrow stopped flow spectrophotometer. The concentrations of lactones **1** were ca 1×10^{-4} mol dm^{-3} and the concentration of sodium hydroxide was 1.58×10^{-2} mol dm^{-3}. The UV-VIS absorption spectra were recorded on a HITACHI 2001 spectrophotometer. The dioxan employed was declared as extra pure (Merck).

IR measurements

The IR spectra of trichloromethane solutions of compounds **1** were recorded on a Zeiss Specord M-80 spectrometer at room temperature using NaCl cells of 0.01 cm thickness. The concentrations of compounds studied were 0.012 mol dm^{-3}. Peak positions were referenced to polystyrene standard spectra. The absorption intensities of the Fermi doublet components were determined after mathematical deconvolution and separation of overlapping bands. Curve analysis was carried out using a digital curve-fitting procedure. The trichloromethane used was of spectroscopic purity (Merck).

Table 9 Physical properties of compounds **1**

Compound	M.p./°C	Recryst. solvent	Formula
1a (R=2-Br)	129–130°C	Ethanol	$C_{16}H_{10}BrNO_2$
1b (R=2-Cl)	109–111°C	Ethanol	$C_{16}H_{10}ClNO_2$
1c (R=2-I)	146–148°C	Ethanol	$C_{16}H_{10}INO_2$
1d (R=2-OMe)	108–110°C	Ethanol	$C_{17}H_{13}NO_3$
1e (R=2,4-Cl_2)	191–192°C	Benzene	$C_{16}H_9Cl_2NO_2$
1f (R=3-Br)	156–158°C	Ethanol	$C_{16}H_{10}BrNO_2$
1g (R=3-NO_2)	224–226°C	Ethanol	$C_{16}H_{10}N_2O_4$
1h (R=4-OMe)	220–222°C	Ethanol	$C_{17}H_{13}NO_3$
1i (R=4-OBu)	122–124°C	Ethanol	$C_{20}H_{19}NO_3$
1j (R=4-OiBu)	98–101°C	Ethanol	$C_{20}H_{19}NO_3$
1k (R=4-Me)	184–187°C	Ethanol	$C_{17}H_{13}NO_2$
1l (R=4-Br)	187–189°C	Ethanol	$C_{16}H_{10}BrNO_2$

NMR measurements

The ^1H and ^{13}C NMR spectra of compounds **1** were recorded for saturated $CDCl_3$ solutions at 300 K with a Bruker Avance DPX spectrometer working at 200.13 MHz for proton and 50.32 MHz for ^{13}C, respectively. The ^1H NMR chemical shifts were referenced to the signal of $CHCl_3$ (δ = 7.27 ppm) and the ^{13}C NMR shifts to the signal of $CDCl_3$ (δ = 77.23 ppm). In order to assign individual chemical shifts the experimental techniques DQF ^1H, ^1H COSY, APT, DEPT and ^1H, ^{13}C HMQC were employed.

Marián Palcut acknowledges financial support within the frameworks Socrates/Erasmus and Ceepus SK-20.

Received 14 April 2004; accepted 25 August 2004
Paper 04/2462

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Table 10 Elemental analysis (in %) of compounds **1**

Compound	C		H		N		X[a]	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
1b (R=2-Cl)	66.73	67.49	3.55	3.48	4.94	4.87	12.50	12.23
1c (R=2-I)	51.22	51.11	2.69	2.75	3.73	3.77	-	-
1d (R=2-OMe)	73.11	73.69	4.69	4.69	5.02	5.04	-	-
1e (R=2.4-Cl)	60.39	60.16	2.85	2.76	4.40	4.37	22.28	19.67
1f (R=3-Br)	58.55	58.50	3.07	2.99	4.27	4.28	24.35	24.38
1i (R=4-OBu)	74.74	74.97	5.96	6.01	4.36	4.32	-	-
1k (R=4-Me)	77.55	77.00	4.98	4.88	5.32	5.25	-	-

[a]X = Cl, Br.