Neutral hydrolysis and imidazole-catalysed decomposition of bis(4-nitrophenyl) oxalate. 1,1′-Oxalyldiimidazole as an intermediate

Helmi Neuvonen
Department of Chemistry, University of Turku, FIN-20500 Turku, Finland

Neutral hydrolysis and imidazole-catalysed decomposition of a peroxyoxalate chemiluminescence reagent type compound, bis(4-nitrophenyl) oxalate (4-NPO), have been studied in acetonitrile and in acetonitrile–water mixtures. For comparison, the rate coefficients for the neutral hydrolysis of 4-nitrophenyl dichloroacetate have also been measured. The first step of the neutral hydrolysis of 4-NPO apparently proceeds by the $B_{AC}3$ mechanism as evidenced by the solvent isotope effect and by the effect of the solvent composition on the rate coefficient. The second step of the reaction is significantly slower than the first one, presumably owing to the retarding inductive effect of the dissociated carboxylate group. The imidazole-catalysed degradation of 4-NPO proceeds by the successive release of the two 4-nitrophenol groups and includes the formation and decomposition of 1,1′-oxalyldiimidazole. Although the hydrolytic reactivity of 4-NPO and 4-nitrophenyl dichloroacetate are close to each other, the reactivity of imidazole toward 4-NPO is considerably higher than toward 4-nitrophenyl dichloroacetate. The difference in reactivity is possibly due to the neighbouring carbonyl group stabilization of the transition state for the partitioning of an addition intermediate in the direction of the substituted phenoxide ion expulsion in the reaction of 4-NPO.

Electronegatively substituted diaryl oxalates are generally used as chemiluminescence (CL) reagents in trace analysis systems based on peroxyoxalate CL (Scheme 1).[1-5] Despite much research the mechanism of this excitation process is not yet understood.[4-11] The reaction is base-catalysed by weak bases and the catalysis is generally necessary to obtain reproducible results.[4,6,8,11a] A remarkable enhancement in CL intensity has been obtained with imidazole, much better than with several other amines studied as the catalyst.[12] Alvarez *et al.*[8] proposed concurrent nucleophilic and general base catalysis by imidazole for the reaction of hydrogen peroxide and bis(2,4,6-trichlorophenyl) oxalate in a CL process in 75% (v/v) acetonitrile–water. $ImCOCO_2Ar$ formed in the first step was suggested to decompose rapidly to products or to react with H_2O_2 to produce HO_2COCO_2Ar. The rate equation for the decomposition of the latter compound was proposed to consist of terms that are zero and second order in imidazole. Recently Steijger *et al.*[13] reported an increase in the imidazole-catalysed peroxyoxalate CL intensity by the presence of metal ions in 88% (v/v) acetonitrile–water. It was proposed that a metal ion stabilization of the ester–imidazole complex results in the enhancement of the CL intensity. Owing to the complexity manifested in the imidazole-catalysed peroxyoxalate CL systems we decided to attain some basic knowledge of the reaction between imidazole and diaryl oxalates in acetonitrile and in acetonitrile–water mixtures, the solvent system generally used in peroxyoxalate CL detection process. There are only a few reports in the literature concerning the kinetics of nucleophilic reactions of amines with oxalic acid esters.[14-16] We recently studied the hydrolytic decomposition of an efficient CL reagent, bis(2,4-dinitrophenyl) oxalate in aqueous acetonitrile.[17] A less reactive derivative, bis(4-nitrophenyl) oxalate (4-NPO) was used in the present work. Both the neutral hydrolysis and the reaction with imidazole were studied. For comparison, rate coefficients for the neutral hydrolysis of 4-nitrophenyl dichloroacetate were also determined.

$$ArOCOCO_2Ar + H_2O_2 \longrightarrow \text{Intermediate(s)} + \text{Products}$$
$$\text{Intermediate(s)} + \text{Flu} \longrightarrow \text{Flu}^* + \text{Products}$$
$$\text{Flu}^* \longrightarrow \text{Flu} + h\nu$$

Scheme 1

Experimental

Materials

Bis(4-nitrophenyl) oxalate (4-NPO) was prepared by the method of Rauhut *et al.*[4a] and recrystallized from acetonitrile, mp 268.5–270.5 °C (lit.,[4a] 240–242 °C). 4-Nitrophenyl acetate and 4-nitrophenyl dichloroacetate were prepared as described previously.[18,19] The melting points were determined on a Büchi 510 capillary melting point apparatus and are uncorrected. Imidazole (Schuchardt) was recrystallized from benzene. 1,1′-Oxalyldiimidazole (Aldrich) and acetonitrile (Merck, gradient grade for chromatography) were used as received. Heavy water was from *Norsk hydro-elektrisk kvaelstoffaktieselskab* (99.8% D_2O).

Kinetics

Reaction rates for the neutral hydrolysis and for the imidazole-catalysed decomposition of 4-NPO or 4-nitrophenyl dichloroacetate were determined by following the increase in UV absorption at 310 nm owing to the formation of 4-nitrophenol. The hydrolysis of 1,1′-oxalyldiimidazole as well as that of a transient intermediate formed in the reaction between imidazole and 4-NPO was followed by observing the decrease in UV absorption at 234 nm. A Gilford 2600 spectrophotometer equipped with a Gilford Thermoset Temperature Controller was used. The temperature was accurate to ± 0.1 °C during the measurements. The reactions were started by addition of a solution of the substrate in acetonitrile (5–100 mm^3) into the kinetic solution (0.4–1 cm^3) contained in a 10 cm^3 flask. The reaction solution was shaken thoroughly, 250 mm^3 of the solution was transferred to a microcell (300 mm^3), and the cell was quickly placed into the thermostatted cell compartment of the spectrophotometer. The absorbance changes were recorded with a printer. The initial concentration of the substrate used in the kinetic solutions was *ca.* 5–8 $\times 10^{-5}$ mol dm^{-3} for the esters and *ca.* 1 $\times 10^{-4}$ mol dm^{-3} for 1,1′-oxalyldiimidazole. The first-

Table 1 First-order rate coefficients (k_{obs}) for the hydrolysis of bis-(4-nitrophenyl) oxalate (4-NPO) and 4-nitrophenyl dichloroacetate (4-NPdiClAc) in acetonitrile–water mixtures at 298.2 K

	$k_{obs}/10^{-3}$ s^{-1}	
$[H_2O]$/mol dm^{-3}	4-NPO[a]	4-NPdiClAc[a]
41.7		8.94 ± 0.01
39.7	17.8 ± 0.2	6.90 ± 0.07
33.3		2.49 ± 0.02
31.7	5.82 ± 0.06	2.05 ± 0.02
27.8		1.26 ± 0.005
26.5	3.32 ± 0.06	1.12 ± 0.001
	1.54[b] ± 0.11	0.37[b] ± 0.01
19.4		0.51 ± 0.002
18.5	1.48 ± 0.04	0.46 ± 0.003
13.2	0.83 ± 0.01	
10.6	0.51 ± 0.01	

[a] The rate coefficients are mean values of three to five determinations and the error is a standard deviation. [b] In 26.5 mol dm^{-3} D_2O in acetonitrile.

order rate coefficients were determined by the method of Guggenheim.[20] For the neutral hydrolysis as well as for the imidazole-catalysed decomposition of the esters the standard deviations of the individual rate coefficients k_{obs} were small, 0.2–0.6%, and good linear plots ln $(A_\infty - A_t)$ *vs.* time ($r \geq 0.9999$ over 3 $t_{\frac{1}{2}}$) were obtained. The k_{obs} values were reproducible to within 1–5%. For the hydrolysis of 1,1′-oxalyldiimidazole or for that of the transient intermediate formed in the reaction between imidazole and 4-NPO the standard deviations of the individual rate coefficients were large, up to 5%. It is assumed that the decrease in UV absorption in these reactions represents two consecutive processes (see Discussion), and their rate coefficients are similar. Nevertheless, the calculated rate coefficients are only used to show that their values for the transient intermediate formed in the reaction between imidazole and 4-NPO are comparable to the values determined for the authentic 1,1′-oxalyldiimidazole.

Results and discussion

Neutral hydrolysis

The rate coefficients measured for the hydrolysis of 4-NPO (Table 1) refer to the release of the first 4-nitrophenol group. The second step of the reaction is considerably slower than the first one. For instance, in 31.7 mol dm^{-3} H_2O in acetonitrile where the k_{obs} value is 5.82×10^{-3} s^{-1} ($t_{\frac{1}{2}} \approx 2$ min), the UV spectrum recorded after 10 half-lives was still unchanged after 12 h. Further, with a 4-NPO concentration of 3×10^{-5} mol dm^{-3}, the UV spectrum after the reaction was identical with that for a solution containing 3×10^{-5} mol dm^{-3} 4-nitrophenol and 3×10^{-5} mol dm^{-3} 4-nitrophenyl acetate. The latter compound satisfactorily mimics the half-hydrolysed 4-NPO. The neutral hydrolysis of oxalic acid diesters is usually shown to proceed in two steps (Scheme 2).[9,14,15,21] The hydrolysis of dimethyl

$$ROCOCO_2R + H_2O \xrightarrow{k_1} ROCOCO_2H + ROH$$

$$ROCOCO_2H + H_2O \xrightarrow{k_2} HOCOCO_2H + ROH$$

Scheme 2

oxalate and methyl hydrogen oxalate occurs at approximately the same rate[21] while for the hydrolysis of some diaryl oxalates the first step has been reported to be faster than the second one.[9] For the hydrolysis of bis(2,4-dinitrophenyl) oxalate we have recently proposed a reaction mechanism where the hydrolysis of the first ester group by the $B_{AC}3$ mechanism is followed by a fast decomposition of 2,4-dinitrophenyl hydrogen oxalate through successive decarboxylation and decarbonylation processes.[17] The deuterium oxide isotope effects, k_{H_2O}/k_{D_2O}, 2.2 and 3.0, respectively, are obtained for the hydrolysis of 4-NPO and 4-nitrophenyl dichloroacetate (*cf.* Table 1). These values indicate a rate-limiting proton transfer being consistent with a mechanism, usual for alkyl, halogenoalkyl and aryl carboxylates, where a molecule of water acts as a general base assisting the addition of a second molecule of water to the ester carbonyl.[22,23] The notation $B_{AC}3$ is used for that reaction mechanism.[24] This mechanism has been suggested earlier for the hydrolysis of 4-nitrophenyl dichloroacetate[25] and also for that of ethyl 2-nitrophenyl oxalate in aqueous solution.[15] Fig. 1 shows the effect of solvent composition on the hydrolysis of 4-NPO and 4-nitrophenyl dichloroacetate as well as on the hydrolysis of some esters which are known to be hydrolysed by the $B_{AC}3$ mechanism.[17,26,27] The values for the hydrolysis of diphenyl oxalate are also included.[28] The plots for the oxalic acid esters are very similar to those for monocarboxylic acid esters. As noted above, the $B_{AC}3$ mechanism has been verified for the first hydrolysis step of bis(2,4-dinitrophenyl) oxalate.[17] It is reasonable to suggest the $B_{AC}3$ mechanism also for the first hydrolysis step of 4-NPO.

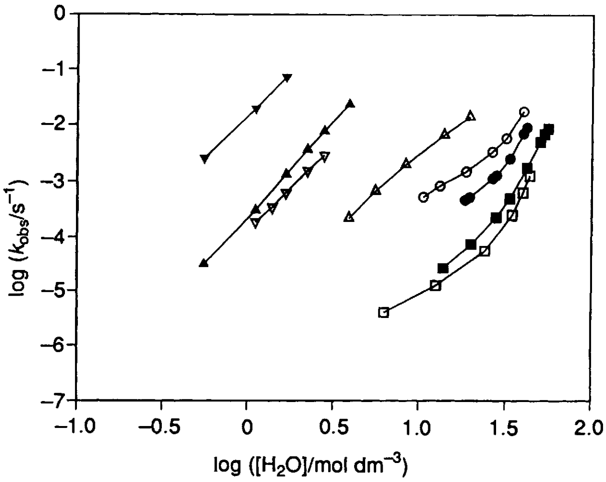


Fig. 1 Plots of log k_{obs} *vs.* log $[H_2O]$ for the neutral hydrolysis of 4-NPO (○) (this study), 4-nitrophenyl dichloroacetate (●) (this study), diphenyl oxalate (□) (ref. 28), methyl trifluoroacetate (■) (ref. 26), phenyl trifluoroacetate (△) (ref. 27), 4-nitrophenyl trifluoroacetate (▲) (ref. 27), 2,4-dinitrophenyl trifluoroacetate (▼) (ref. 27) and bis(2,4-dinitrophenyl) oxalate (▽) (ref. 17) in acetonitrile–water mixtures at 298.2 K

Orosz[9] has reported that for the hydrolysis of several symmetrical and unsymmetrical diaryl oxalates in a 5 : 2 mixture of tetrahydrofuran and water at pH 4.0, the first step of the reaction is at least 100 times faster than the second one. This was found to agree with the result of Bruice and Holmquist[15] that the rates of hydrolysis of ethyl 2-nitrophenyl oxalate and 2-nitrophenyl hydrogen oxalate in water differ by at least two orders of magnitude. In fact, however, Bruice and Holmquist[15] have observed the rate coefficients 2.23×10^{-2} and 9.65×10^{-3} s^{-1}, respectively, for the hydrolysis of ethyl 2-nitrophenyl oxalate and 2-nitrophenyl hydrogen oxalate while the rate coefficient for the hydrolysis of 2-nitrophenyl oxalate anion differs by three orders of magnitude. The similar size of the electronegativities of $-CO_2H$ and $-CO_2Et$ explains the similarity in the rate coefficients for 2-nitrophenyl hydrogen oxalate and ethyl 2-nitrophenyl oxalate. On the other hand, the decreased reactivity of the 2-nitrophenyl oxalate anion is in agreement with the low electronegativity of the $-CO_2^-$ group.[15,29,30] The methyl oxalate anion is also hydrolysed in water at a very low rate compared with methyl hydrogen

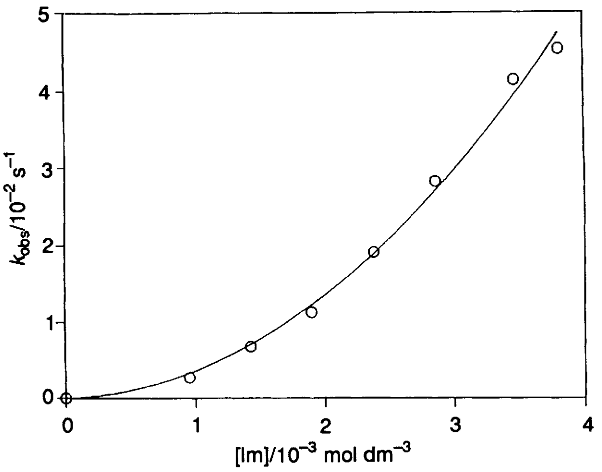
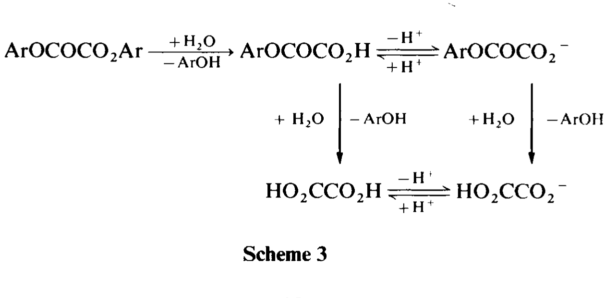


Fig. 2 Plot of the observed rate coefficients *vs.* the imidazole concentration for the release of the second 4-nitrophenol group in the decomposition of 4-NPO in acetonitrile at 298.2 K

oxalate.[21] Although the electronegativity of the nitro-substituted $-CO_2Ar$ group obviously is somewhat higher than that for $-CO_2R$ or $-CO_2H$, the reactivity of 4-nitrophenyl hydrogen oxalate should not be much lower than that of bis(4-nitrophenyl) oxalate. In the consecutive methanolysis process in 1.67 mol dm^{-3} methanol in acetonitrile, the ratio of the rate coefficients for bis(2,4-dinitrophenyl) oxalate and 2,4-dinitrophenyl methyl oxalate is *ca.* 60.[17] Accordingly, it is obvious that under the reaction conditions used (ref. 9 and this work) the aryl hydrogen oxalate formed in the first reaction step is in the anionic form.

As expected, the increase in rate of the second reaction step was observed while the first step stayed unchanged when trifluoroacetic acid was added to the reaction solution in the hydrolysis of 4-NPO. For example, the k_{obs} value 5.38 × 10^{-3} s^{-1} in 31.3 mol dm^{-3} water in acetonitrile with 0.013 mol dm^{-3} trifluoroacetic acid (5 × 10^{-5} mol dm^{-3} of 4-NPO) fits well the log k_{obs} *vs.* log [H_2O] plot in Fig. 1. The release of the first 4-nitrophenol group was followed by an only somewhat slower release of the second one. The k_{obs} value for the second step was 1.63 × 10^{-4} s^{-1}. It is obvious that with the acidities used 4-nitrophenyl hydrogen oxalate is still present partly as the 4-nitrophenyl oxalate anion, and the total process may be described by Scheme 3.[21] For 2-nitrophenyl hydrogen oxalate the pK_a value in water is 0.38.[15] The acidity of 4-nitrophenyl hydrogen oxalate must be close to that. Hence, the 4-nitrophenyl oxalate anion will be completely protonated only at a moderately high acid concentration.



Scheme 3

Imidazole-catalysed decomposition of 4-NPO

The reactivity of 4-NPO toward water is close to that of 4-nitrophenyl dichloroacetate in acetonitrile–water mixtures (Table 1). On the contrary, the reaction of imidazole with 4-NPO is much faster than its reaction with 4-nitrophenyl dichloroacetate.[19] The rate coefficients (Table 2) refer to the release of the second 4-nitrophenol group of 4-NPO, and it was found only that the release of the first 4-nitrophenol group is at least 10 times as fast as that of the second one. The upward curvature of the line in Fig. 2 indicates a second-order dependence on the amine concentration, and this is verified by the plot shown in Fig. 3. The first-order term in imidazole is insignificant and the reaction follows the rate eqn. (1). The

Table 2 First-order rate coefficients ($k_{obs}{}^a$) for the reaction of imidazole with bis(4-nitrophenyl) oxalate in acetonitrile or in acetonitrile–water mixture with [H_2O] = 0.44 mol dm^{-3} at 298.2 K. The rate coefficients determined refer to the release of the second 4-nitrophenol group

[Imidazole]/10^{-3} mol dm^{-3}	$k_{obs}{}^b$/10^{-3} s^{-1}	$k_{obs}{}^c$/10^{-3} s^{-1}
0.952	2.68 ± 0.06	
1.20		3.18 ± 0.07
1.43	6.78 ± 0.04	
1.60		6.04 ± 0.06
1.90	11.2 ± 0.12	
2.38	19.1 ± 0.3	
2.40		14.4 ± 0.3
2.86	28.2 ± 0.5	
3.20		24.8 ± 0.8
3.47	41.4 ± 0.1	

[a] The rate coefficients are mean values of three to five determinations and the error shown is a standard deviation. [b] In acetonitrile. [c] In acetonitrile–water with [H_2O] = 0.44 mol dm^{-3}.

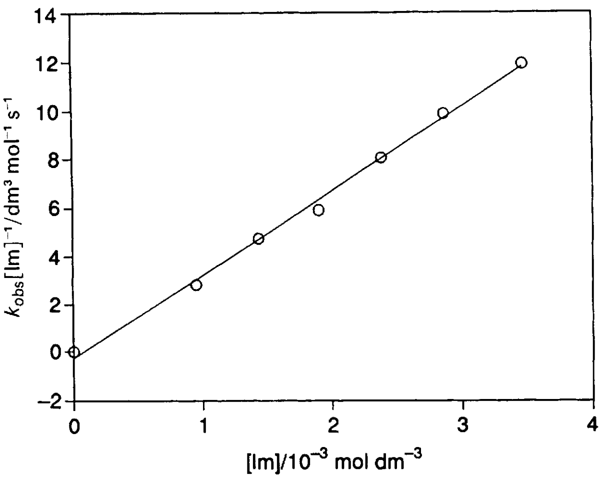


Fig. 3 Plot of k_{obs}/[Imidazole] *vs.* [Imidazole] for the release of the second 4-nitrophenol group in the decomposition of 4-NPO in acetonitrile at 298.2 K

$$k_{obs} = k'[\text{Imidazole}]^2 \qquad (1)$$

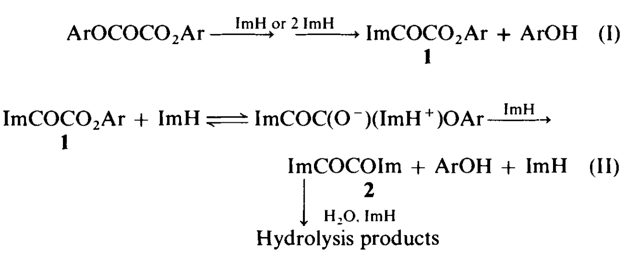
value of k' is (3500 ± 100) dm^6 mol^{-2} s^{-1} in acetonitrile and (2500 ± 100) dm^6 mol^{-2} s^{-1} in acetonitrile–water containing 0.44 mol dm^{-3} of water. Both the uncatalysed and general base-catalysed nucleophilic reactions of imidazole have been detected previously in the reactions of imidazole with 4-nitrophenyl acetate,[18] chloroacetate[19] and dichloroacetate[19] in acetonitrile and in aqueous acetonitrile with a low content of water. With 4-nitrophenyl trifluoroacetate the reaction first-order in imidazole is general base-catalysed hydrolysis.[18] Beside this reaction the general base-catalysed nucleophilic reaction of imidazole is still observed. The overall third-order process in the reactions of amines with acyl derivatives in aprotic solvents can usually be attributed to the general base-catalysed nucleophilic reaction of the amine.[19,31–34] The UV spectra of the reaction of imidazole with 4-NPO showed the occurrence of a transient intermediate absorbing in the region 230–250 nm. The decrease in the UV absorption in this region continued slowly although the increase in the absorption due to the formation of 4-nitrophenol

Table 3 First-order rate coefficients at different imidazole concentrations for the decomposition of 1,1′-oxalyldiimidazole (1,1′-OdiIm) and for that of the transient intermediate formed in the reaction of imidazole with bis(4-nitrophenyl) oxalate in acetonitrile–water with $[H_2O] = 0.44$ mol dm^{-3} at 298.2 K

	k_{obs}[a]/10^{-3} s^{-1}	
[Imidazole]/10^{-3} mol dm^{-3}	1,1′-OdiIm	Intermediate
0.8	1.26 ± 0.11	*b*
1.6	1.83 ± 0.05	1.60 ± 0.04
2.4	2.33 ± 0.04	2.14 ± 0.07
4.0	2.59 ± 0.11	2.60 ± 0.02
5.6	3.76 ± 0.21	3.96 ± 0.25

[a] The rate coefficients are mean values of three to four determinations and the errors are standard deviations. [b] Not measured owing to the unfavourable ratio of the rate coefficients for the formation and the decomposition of the intermediate.

at *ca.* 310 nm was finished. The rate of the decomposition of the intermediate was dependent on the imidazole concentration. In the light of these results Scheme 4 may be proposed for the



$$\mathrm{ArOCOCO_2Ar} \xrightarrow{\mathrm{ImH\ or\ 2\,ImH}} \underset{\mathbf{1}}{\mathrm{ImCOCO_2Ar}} + \mathrm{ArOH} \qquad \mathrm{(I)}$$

$$\underset{\mathbf{1}}{\mathrm{ImCOCO_2Ar}} + \mathrm{ImH} \rightleftharpoons \mathrm{ImCOC(O^-)(ImH^+)OAr} \xrightarrow{\mathrm{ImH}} \underset{\mathbf{2}}{\mathrm{ImCOCOIm}} + \mathrm{ArOH} + \mathrm{ImH} \qquad \mathrm{(II)}$$

$$\mathbf{2} \ \big\downarrow{\scriptstyle \mathrm{H_2O,\ ImH}} \ \text{Hydrolysis products}$$

Scheme 4

whole process. The step referring to the release of the first 4-nitrophenol group and to the formation of the oxalyl derivative (**1**) is fast compared with the second reaction step. The observed rate coefficients (Table 2) refer to the nucleophilic reaction of imidazole toward the ester group of compound **1**. The excellent first-order behaviour of the reaction means that the substrate of this step is not decomposed through a parallel hydrolysis process without the release of 4-nitrophenol. In accordance with the reactions of monocarboxylic esters with amines in aprotic solvents, the base-catalysed breakdown of the zwitterionic addition intermediate supposedly is the rate-limiting step of this reaction.[18,19,31b,c,32] The k' term in 0.44 mol dm^{-3} water in acetonitrile is *ca.* 30% lower than that in acetonitrile. A decrease of the same extent by addition of water (0.56 mol dm^{-3}) into acetonitrile was detected for the general base-catalysed nucleophilic reaction of imidazole with 4-nitrophenyl chloroacetate or dichloroacetate.[19] The observed decrease in absorption in the region 230–250 nm after the 4-nitrophenol release is attributed to the hydrolysis of 1,1′-oxalyldiimidazole (**2**). The hypothesis of the structure of the intermediate is supported by the fact that 1-acetylimidazole possesses an absorption maximum at 245 nm [35] and 1-oxalylimidazole in the region of 240–260 nm.[15] Further, the rate coefficients both for the hydrolysis of the transient intermediate formed in the reaction between imidazole and 4-NPO and for the hydrolysis of the commercial 1,1′-oxalyldiimidazole were measured in 0.44 mol dm^{-3} water in acetonitrile (Table 3). The equal dependence of the rate coefficients on imidazole concentration in these two cases (Fig. 4) nicely supports the claim of 1,1′-oxalydiimidazole as the intermediate. The slopes of the plots are 0.47 ± 0.06 for 1,1′-oxalyldiimidazole and 0.56 ± 0.09 dm^3 mol^{-1} s^{-1} for the unstable intermediate detected during the reaction. Because nucleophilic attack by imidazole would in this case only result in the reversion of the starting compound, general base catalysis of the hydrolysis of **2** by imidazole is suggested. The observed rate coefficients obviously include two consecutive processes, the hydrolysis of 1,1′-oxalyldiimidazole and that of 1-oxalylimidazole. Although the value of 1,1′-oxalyldiimidazole as a synthetic reagent is well known,[36] its solution kinetics have not been studied so far. The details of the mechanism of the first reaction step (I in Scheme 4) were not clarified in this work. On the basis of the known behaviour of aryl esters of monocarboxylic acids, a general base-catalysed nucleophilic reaction of the amine and therefore a second-order dependence on the imidazole concentration, with or without the first-order term in imidazole, can, however, be assumed.[18,19,31-33]

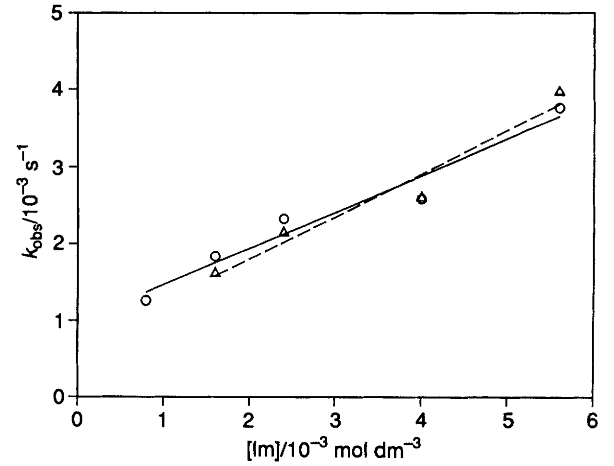
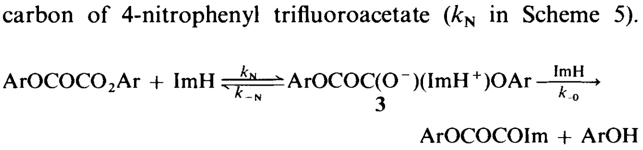


Fig. 4 Plots of the observed rate coefficients *vs.* the imidazole concentration for the imidazole-catalysed hydrolysis of 1,1′-oxalyldiimidazole (○, ——) and for that of the transient intermediate formed during the imidazole-catalysed decomposition of 4-NPO in 0.44 mol dm^{-3} water in acetonitrile at 298.2 K (Δ, – – –)

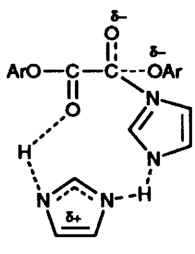
The reactivity of 4-NPO toward imidazole was observed to be at least 10 times that of the oxalyl derivative (**1**). As an example, with an imidazole concentration of 2×10^{-3} mol dm^{-3} in acetonitrile this gives $k_{obs} \geq 0.14$ s^{-1} for 4-NPO. For 4-nitrophenyl dichloroacetate possessing nearly equal hydrolytic reactivity with 4-NPO (Table 1, Fig. 1), the respective calculated value of k_{obs} is only 2.4×10^{-3} s^{-1} (k_1 and k_2 from ref. 19). With the aid of the known rate coefficients for the reaction of imidazole with a very strongly activated substrate, 4-nitrophenyl trifluoroacetate, a calculated value of 1.5×10^{-2} s^{-1} is obtained for k_{obs} (k_1 and k_2 from ref. 18). By extrapolation of the plots in Fig. 1, a value of 500 can be evaluated for the ratio k_{obs}(4-nitrophenyl trifluoroacetate)/k_{obs} (4-NPO). Thus the relative rates for the hydrolysis of these two esters indicate that the $O_2N–C_6H_4–OCO–$ group is less electron-withdrawing than the $CF_3–$ group and the reacting acyl carbon in 4-NPO should be less susceptible to nucleophilic attack than is the carbonyl carbon of 4-nitrophenyl trifluoroacetate (k_N in Scheme 5).



$$\mathrm{ArOCOCO_2Ar} + \mathrm{ImH} \underset{k_{-N}}{\overset{k_N}{\rightleftharpoons}} \underset{\mathbf{3}}{\mathrm{ArOCOC(O^-)(ImH^+)OAr}} \xrightarrow[k_{\mathrm{o}}]{\mathrm{ImH}} \mathrm{ArOCOCOIm} + \mathrm{ArOH}$$

Scheme 5

However, the high reactivity of imidazole towards 4-NPO implies that the change of the acyl group from $CF_3–$ to $O_2N–C_6H_4–OCO–$ favours the substituted phenoxide ion expulsion relative to amine expulsion from the tetrahedral intermediate (**3**). This can be explained by hydrogen bonding to the carbonyl oxygen of the non-leaving group as shown in (**4**). Intermolecular hydrogen bonding between ester carbonyl and imidazole *N*-hydrogen has been detected by IR spectroscopy for instance for *trans*-methyl urocanate while the *cis* isomer forms intramolecular hydrogen bonds.[37]



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The relative rates observed for the different reaction steps in the imidazole-catalysed decomposition of 4-NPO and the verification of 1,1′-oxalyldiimidazole as the intermediate are applicable when continuing the study of the mechanism of peroxyoxalate chemiluminescence.

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