Formation of singlet molecular oxygen by the Radziszewski reaction between acetonitrile and hydrogen peroxide in the absence and presence of ketones

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Measurements of the infrared phosphorescence of singlet molecular oxygen ($^1O_2$) at 1270 nm have been used to demonstrate the formation of $^1O_2$ by the Radziszewski reaction between acetonitrile and hydrogen peroxide. The kinetics of the Radziszewski reaction either alone or in the presence of ketones have been studied by this technique. The rate-determining step of the $^1O_2$ formation of the reaction in the absence of ketones was found to be independent of both the concentration of acetonitrile and that of hydrogen peroxide. The kinetic data, the results of the volumetric measurements of the oxygen liberated and the results of the determination of the amount of $^1O_2$ generated by the reaction are consistent with the assumption that the reaction between acetonitrile and hydrogen peroxide occurs *via* the heterolytic decomposition of the intermediate, peroxyacetimidic acid (PAIA), forming 1 mol acetamide and 0.5 mol $^1O_2$ according to the stoichiometric equation: $CH_3CN + H_2O_2 \longrightarrow CH_3C(=O)NH_2 + 0.5\ ^1O_2$. The rate constant of the heterolytic decomposition of PAIA was determined to be $k_8 = 1.2 \times 10^{-3}$ dm^3 mol^{-1} s^{-1} at $T = 30$ °C. From the measurements at different pH values in the range $9.1 < \text{pH} < 12.0$ the pK_a(PAIA) value was estimated to be 11.1 at $T = 30$ °C. The investigation of the reaction between acetonitrile and hydrogen peroxide by using *N*,*N*-dimethyl-4-oxopiperidinium nitrate as catalyst, has unequivocally shown that the rate of $^1O_2$ formation is considerably enhanced by this ketone. For the ketone-catalysed decomposition of PAIA a rate law can be derived showing a first order dependence on the concentration of acetonitrile and hydrogen peroxide at a given pH. In accordance with the observed rate law are the results with acetonitrile in 50% acetone containing a tenfold excess of hydrogen peroxide at pH 8.2 and $T = 60$ °C.

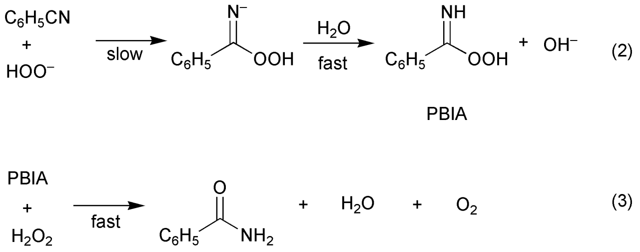
Introduction

The reaction of a nitrile with hydrogen peroxide in mildly alkaline solution to produce an amide, water and oxygen is known as the Radziszewski reaction. In the original paper[1] the overall reaction is given as

$$RCN + 2\,H_2O_2 \longrightarrow RC(=O)NH_2 + H_2O + O_2 \qquad (1)$$

The kinetics of alkaline decomposition of hydrogen peroxide and benzonitrile were first studied by Wiberg.[2] He reported that the rate-determining reaction was the formation of peroxybenzimidic acid (PBIA) from the addition of the perhydroxide (OOH^-) toward the nitrile. It was assumed that the intermediary-generated PBIA oxidizes another molecule of hydrogen peroxide by a successive fast reaction to evolve oxygen and benzamide (Scheme 1).

It was Payne *et al.*[3] who initially developed a method for epoxidation and oxidation using hydrogen peroxide and an organic nitrile under mildly alkaline conditions. Later, Bach *et al.*[4] reported a procedure for the large-scale epoxidation of cyclooctene using the acetonitrile–hydrogen peroxide and the more reactive trichloroacetonitrile–hydrogen peroxide system under biphasic reaction conditions. Today it is generally accepted that the 'oxidation power' of the nitrile–hydrogen peroxide system is caused by the intermediate, peroxycarboximidic acid (PCIA).[5]



Scheme 1

Recently, an efficient ketone-catalysed epoxidation using hydrogen peroxide as primary oxidant in combination with acetonitrile has been developed.[6] Using different ketones as catalysts it was found that trifluoroacetone (CF_3COCH_3) gave the best conversion of *trans*-β-methylstyrene as substrate in the acetonitrile–hydrogen peroxide system.

However, some doubts exist with respect to the generally accepted mechanism of the Radziszewski reaction postulated by Wiberg.[2] Sawaki and Ogata[7] have investigated the kinetics of substituted benzonitriles with hydrogen peroxide in methanol–water solutions and have found that the formation of the peroxycarboximidic acids is *not* rate-determining in contrast to the mechanism of Wiberg.

Wiberg[2] has investigated the mechanism between hydrogen peroxides and benzonitrile and substituted benzonitriles, respectively, in 25–50% acetone–water solutions. At this time it was not known that the heterolytic decomposition of peroxy acids like Caro's acid[8] and peroxycarboxylic acids[9] is efficiently catalysed by ketones through the formation of dioxiranes as

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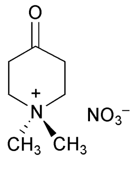
intermediates combined with a change in the mechanism. Whereas the uncatalysed decomposition of a peroxy acid shows a second-order dependence on the concentration of the peroxy acid, the ketone-catalysed decomposition is found to be of first-order with respect to the concentration of the peroxy acid.[8,9]

Our interest in the uncatalysed and the ketone-catalysed decomposition of peroxy acids led us to a reinvestigation of the Radziszewski reaction between acetonitrile and hydrogen peroxide to clarify the mechanism. Furthermore we studied the mentioned reaction in the presence of *N*,*N*-dimethyl-4-oxo-piperidinium nitrate ($DMOP^+ NO_3^-$) as catalyst as well in 50% acetone–water.



$DMOP^+ NO_3^-$

Experimental

Materials

Acetonitrile (Fluka, for UV-spectroscopy), acetone (Aldrich, HPLC grade) and 30% hydrogen peroxide (Merck, pract.) were used as received. Reactions were carried out in buffered aqueous solutions in the pH region 8–12 in the presence of Dequest 2066 (Monsanto) as effective metal-chelating agent. H_2O was distilled twice and the buffer components were of the highest grade as previously described.[8f] $DMOP^+ NO_3^-$ was synthesized by the literature procedure[10] followed by anionic exchange of the requisite iodide salt with silver nitrate.[11]

Singlet oxygen infrared emission measurements

The $^1O_2$ phosphorescence at $\lambda = 1270$ nm was recorded with a laboratory made near-infrared luminescence (IRL) spectrometer.[12–15] For the intensity of the $^1O_2$ phosphorescence emission, I_p, eqn. (4) holds,[14] where $c = (1.0 \pm 0.1) \times 10^{11}$ mV dm^3 mol^{-1} s is a constant of the IRL spectrometer, k_p is the rate constant of the

$$I_p = ck_p\tau_\Delta \frac{d[^1O_2]}{dt} \tag{4}$$

$^1O_2$ phosphorescence emission (in water: $k_p = 0.21$ s^{-1})[15] and τ_Δ is the lifetime of $^1O_2$ (in water: $\tau_\Delta = 3.1$ μs).[16] The errors of k_p and τ_Δ, respectively, amount to about 10%. d[$^1O_2$]/d*t* denotes the rate of singlet oxygen formation.

The concentration of $^1O_2$ can be calculated according to eqn. (5), where *C* represents the product $ck_p\tau_\Delta = (6.5 \pm 1.3) \times 10^4$ mV dm^3 mol^{-1} s^{-1}.

$$[^1O_2] = \frac{1}{C}\int_{t=0}^{t} I_p(t)dt \tag{5}$$

Reactions were carried out in thermostatted 1 cm quartz cuvettes at constant temperature. To the buffer/Dequest 2066/acetonitrile solutions and to the buffer/Dequest 2066/acetonitrile/ketone solutions, respectively, 30% hydrogen peroxide was added by a micro syringe. Vigorous stirring was conducted. The initial concentrations at time $t = 0$ of the used educts are given in the legends of the figures or in the text.

Results and discussion

A Investigation of the CH_3CN–H_2O_2 system in water in the absence of ketones

The question of whether the oxygen evolved in the Radziszewski reaction is generated as $^1O_2$ has been investigated already using chemical traps.[7,17] However, neither Sawaki and Ogata[7] nor McKeown and Waters[17] could prove the generation of $^1O_2$. In contrast to this result our preliminary tests[18] with the IRL technique have unequivocally shown that in the reaction of acetonitrile with hydrogen peroxide $^1O_2$ is formed, whereby the generation of $^1O_2$ strongly depends on pH.

A.1 $^1O_2$ Phosphorescence intensity as a function of time. Fig. 1 shows the $^1O_2$ phosphorescence intensity $I_p(t)$ as a function of time observed for the reaction of equimolar quantities of acetonitrile and hydrogen peroxide at pH 9.9. For comparison no $^1O_2$ signal was observed at pH 8.2 using the acetonitrile–hydrogen peroxide system. The plot of $(I_p(t)/\text{mV})^{-1/2}$ *versus* time resulted in a straight line [inset of Fig. 1] indicating that the rate-determining step for the $^1O_2$ generation is of second-order[8f] (*vide infra*). At first sight this result seems to confirm the mechanism postulated by Wiberg.[2] According to this mechanism the rate-determining step should show at a given pH a first-order dependence on the concentration of the nitrile and hydrogen peroxide, *i.e.* the rate-determining step should be of second-order.

Consequently, when hydrogen peroxide or acetonitrile is used in a large excess the rate-determining step should be pseudo-first-order with respect to the concentration of acetonitrile and of hydrogen peroxide, respectively. If this holds true then the plot of ln $(I_p(t)/\text{mV})$ *versus* time must result in a straight line. To prove this prediction we have performed measurements using one of the educts in a large excess.

Fig. 2 reveals the $I_p(t)$ curve obtained for the reaction at pH 10.5 with a tenfold excess of hydrogen peroxide. In contrast to the expectation the plot of ln $(I_p(t)/\text{mV})$ *versus* time does *not* yield a straight line (it is not shown). But as shown in the inset of Fig. 2 the plot of $(I_p(t)/\text{mV})^{-1/2}$ *versus* time is found to be linear, *i.e.* also in the presence of a tenfold excess of hydrogen peroxide a second-order reaction is observed for the generation of $^1O_2$.

As Fig. 3 demonstrates a similar result is obtained for the reaction with a tenfold excess of acetonitrile. Obviously the results found for the reaction between acetonitrile and hydrogen peroxide in water are in contrast to the mechanism of Wiberg.[2] Our results suggest that neither acetonitrile nor hydrogen peroxide is involved in the rate-determining step of the $^1O_2$-generation and as a consequence the formation of the intermediate, PAIA, cannot be the rate-determining step, in agreement with the observation made by Sawaki and Ogata.[7]

Considering the fact that $^1O_2$ is evidently formed *via* a rate-determining second-order step independently of the ratio of the concentrations of acetonitrile and hydrogen peroxide, it can be deduced that $^1O_2$ is generated by the heterolytic decomposition of two molecules of PAIA, *i.e.* by a mechanism generally observed for the decomposition of inorganic peroxy acids and peroxycarboxylic acids, respectively.[19] However, in this case only one molecule of hydrogen peroxide should be involved in the generation of $^1O_2$. Thus for the stoichiometric equation of the reaction between acetonitrile and hydrogen peroxide eqn. (6) should be valid.

$$CH_3CN + H_2O_2 \longrightarrow CH_3C(=O)NH_2 + 1/2\ ^1O_2 \tag{6}$$

A.2 Determination of the amount of oxygen. Neither Radziszewski[1] nor Wiberg[2] has reported quantitative measurements of the oxygen evolved in the reaction between benzonitrile and hydrogen peroxide. Up to now only McIsaac *et al.*[20]

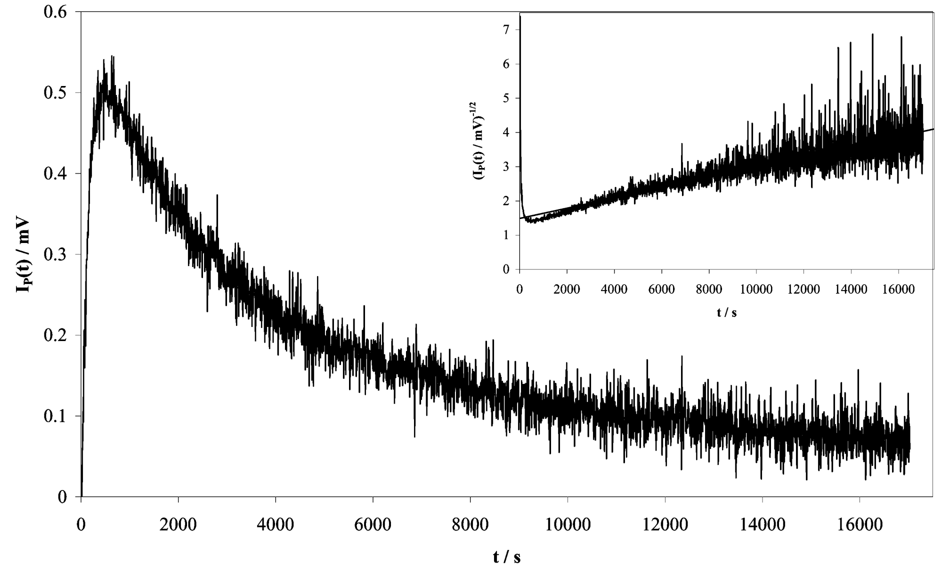


Fig. 1 $I_p(t)$ as a function of time for the reaction between acetonitrile and hydrogen peroxide. Conditions: $[CH_3CN](0) = [H_2O_2](0) = 0.94$ mol dm^{-3}, [Dequest] = 1.0×10^{-4} mol dm^{-3}, pH = 9.9 and T = 30 °C. The inset shows the corresponding plot of $(I_p(t)/\text{mV})^{-1/2}$ *versus* time (sl = 1.49×10^{-4} s^{-1}; int = 1.49).

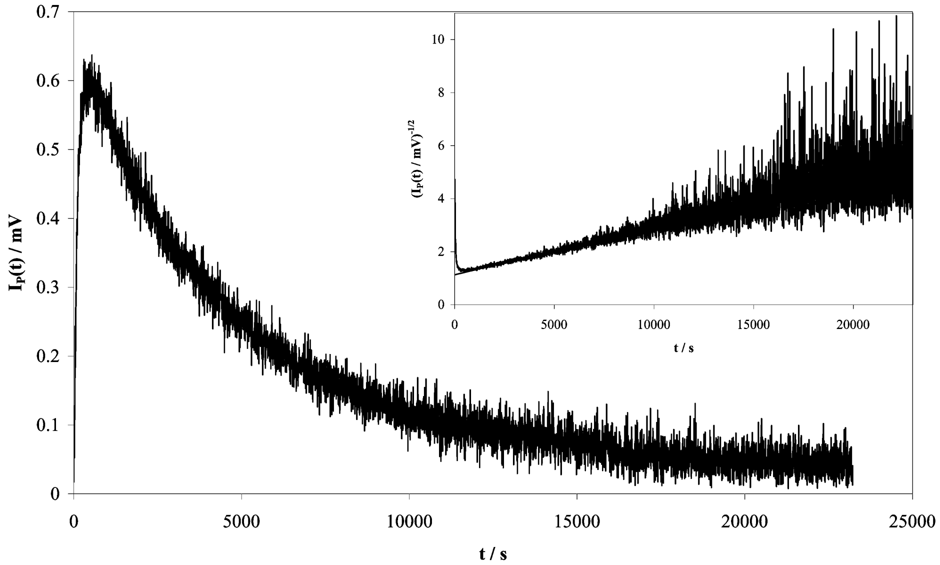


Fig. 2 $I_p(t)$ as a function of time for the reaction between acetonitrile and hydrogen peroxide. Conditions: $[CH_3CN](0) = 0.5$ mol dm^{-3}, $[H_2O_2](0) =$ 5.0 mol dm^{-3}, [Dequest] = 1.0×10^{-4} mol dm^{-3}, pH = 10.5 and T = 30 °C. The inset shows the corresponding plot of $(I_p(t)/\text{mV})^{-1/2}$ *versus* time; (sl = 1.82×10^{-4} s^{-1}; int = 1.13).

have conducted gas volumetric measurements of the evolved oxygen from the reaction of *p*-cyanobenzoic acid with hydrogen peroxide. The authors reported that these measurements would confirm the stoichiometry of eqn. (1). However, in this study ethylenediaminetetraacetate (EDTA) was used as chelating agent with [EDTA] = 8×10^{-5} mol dm^{-3}. It is of interest that a significant curvature of the second-order and the first-order plots of the given data was observed. It seems that the decomposition of the *in-situ* generated peroxyimidic acid is extraordinarily sensitive to transition-metal ions and some radical decomposition of the peroxyimidic acid may have occurred using EDTA as chelating agent and resulted in an enhancement of the liberated oxygen.

To prove the prediction of eqn. (6) we have carried out gas volumetric measurements according to the procedure described by Rebek *et al.*[21] In the experiments at pH 9.9 concentrations of $[CH_3CN](0) = 0.94$ mol dm^{-3} and of $[H_2O_2](0) = 9.4$ mol dm^{-3} were employed. Since the velocity of oxygen liberation was very low at T = 30 °C the experiments were performed at T = 60 °C. Under these conditions reproducible values were obtained. In accordance with eqn. (6) it was found that 0.52 ± 0.06 mol of oxygen is generated from 1 mol acetonitrile.

Additionally, the amount of $^1O_2$ was determined with the IRL technique. The measurement was also carried out at pH 9.9 and at T = 60 °C using 0.5 mol dm^{-3} acetonitrile and 5.0 mol dm^{-3} hydrogen peroxide in solution. The $^1O_2$ phosphorescence curve obtained is depicted in Fig. 4. The area under the curve corresponds to the amount of the evolved $^1O_2$. The area was estimated to be (18914 ± 4%) mV s and according to eqn. (5) with $C = 6.5 \times 10^4$ mV dm^{-3} mol^{-1} s for the concentration of $^1O_2$ a value of $[^1O_2] = 0.29 \pm 0.05$ mol dm^{-3} is obtained. From this value and the initial concentration $[CH_3CN](0) = 0.5$ mol dm^{-3} it follows that the efficiency $\eta = [^1O_2]/[CH_3CN](0)$ amounts to about 0.58 ± 0.10. This value is consistent with eqn. (6) and indicates that the oxygen evolved in the reaction between acetonitrile and hydrogen peroxide is quantitatively generated as $^1O_2$.

It should be mentioned that the amount of $^1O_2$ estimated from the area under the $I_p(t)$ curve of Fig. 2 observed at T = 30 °C is smaller than the amount of $^1O_2$ expected according

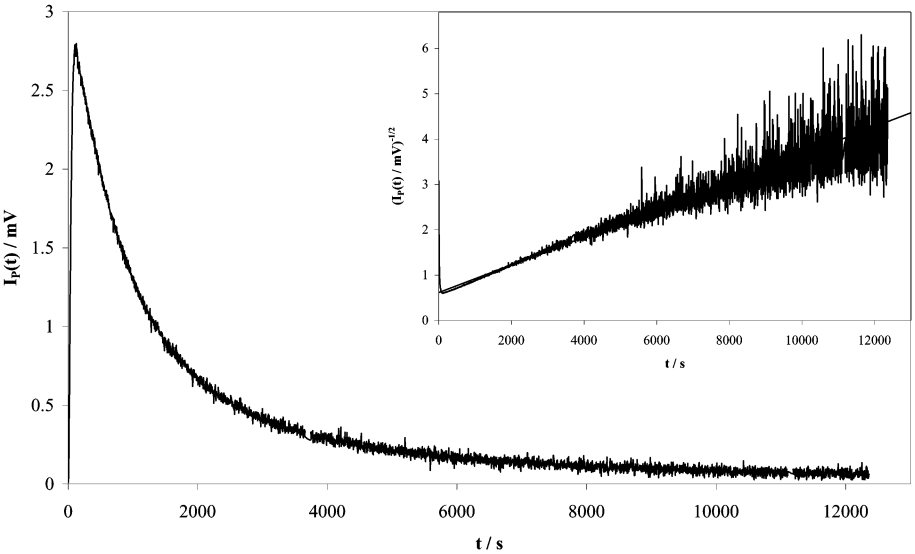


Fig. 3 $I_p(t)$ as a function of time for the reaction between acetonitrile and hydrogen peroxide. Conditions: $[CH_3CN](0) = 5.0$ mol dm^{-3}, $[H_2O_2](0) = 0.5$ mol dm^{-3}, [Dequest] = 1.0×10^{-4} mol dm^{-3}, pH = 12.0 and T = 30 °C. The inset shows the corresponding plot of $(I_p(t)/\mathrm{mV})^{-1/2}$ *versus* time; (sl = 2.83×10^{-4} s^{-1}; int = 0.69).

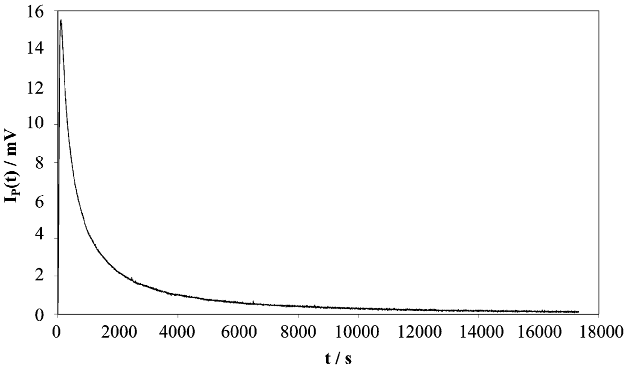
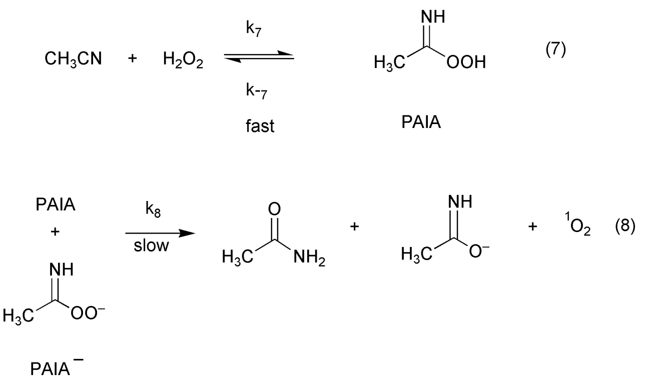


Fig. 4 $I_p(t)$ as a function of time for the reaction between acetonitrile and hydrogen peroxide. Conditions: $[CH_3CN](0) = 0.5$ mol dm^{-3}, $[H_2O_2](0) = 5.0$ mol dm^{-3}, [Dequest] = 1.0×10^{-4} mol dm^{-3}, pH = 9.9 and T = 60 °C. $_0\int^{17000} I_p(t)\,dt = 18914$ mV s (±4%).

to eqn. (6). In this connection it must be noted that in aqueous solution $^1O_2$ can only be detected by our IRL spectrometer, if the rate of $^1O_2$ formation amounts to $d[^1O_2]/dt \geq 3.0 \times 10^{-6}$ mol dm^{-3} s^{-1}. Thus it seems likely that at T = 30 °C after a longer reaction time the rate of $^1O_2$ formation becomes smaller than 3.0×10^{-6} mol dm^{-3} s^{-1} although the reaction is not completed.

A.3 The mechanism of the Radziszewski reaction between CH_3CN and H_2O_2.

On the basis of our results presented so far for the reaction between acetonitrile and hydrogen peroxide the mechanism given in Scheme 2 can be deduced.



Scheme 2

In this mechanism the bimolecular reaction of PAIA with the corresponding peroxy acid anion, PAIA$^-$, is assumed to be the rate-determining step [eqn. (8)]. Furthermore the perhydration equilibrium (7) is postulated to occur very fast.

Of course the HOO$^-$ is a better nucleophile than the undissociated H_2O_2, especially at pH = pK_a = 11.7, so that it is considerably more effective than the latter in carrying out the addition step to acetonitrile forming PAIA$^-$. However, this has no influence on the rate of $^1O_2$ formation, because HOO$^-$ is also not involved in the rate-determining step.

On the basis of the result that at a given pH the values of the experimental rate constants, k_{exp}, obtained at different concentrations of hydrogen peroxide agree very well within the error limits (*vide infra*), it can be assumed that equilibrium (7) is practically shifted to [PAIA]. In this case eqn. (9) can be derived for the formation of singlet oxygen:

$$\frac{d[^1O_2]}{dt} = -\frac{1}{2}\frac{d[\mathrm{PAIA}]_T}{dt} = k_{exp}[\mathrm{PAIA}]_T^2 \qquad (9)$$

where k_{exp} is defined by eqn. (10)

$$k_{exp} = k_8 F_H \qquad (10)$$

k_8 denotes the second-order rate constant of the rate-determining step. The factor F_H is a constant at a given pH and is defined by eqn. (11)

$$F_H = \frac{[H^+]K_a(\mathrm{PAIA})}{\{[H^+] + K_a(\mathrm{PAIA})\}^2} \qquad (11)$$

where K_a(PAIA) represents the dissociation constant of PAIA. F_H describes the pH dependence of the rate of $^1O_2$ formation. Finally, $[\mathrm{PAIA}]_T$ = [PAIA] + [PAIA$^-$] denotes the total concentration of peroxyacetimidic acid. For $[\mathrm{PAIA}]_T$ the following relations should be valid:

i) for $[CH_3CN](0) = [H_2O_2](0)$: $[\mathrm{PAIA}]_T(0) = [CH_3CN](0)$ or $[\mathrm{PAIA}]_T(0) = [H_2O_2](0)$

ii) for $[CH_3CN](0) \gg [H_2O_2](0)$: $[\mathrm{PAIA}]_T(0) = [H_2O_2](0)$

iii) for $[H_2O_2](0) \gg [CH_3CN](0)$: $[\mathrm{PAIA}]_T(0) = [CH_3CN](0)$.

On the basis of these assumptions eqn. (12) can be derived for the $^1O_2$ phosphorescence intensity $I_p(t)$:[8f]

$$I_p(t) = Ck_{exp}[\mathrm{PAIA}]_T(0)\frac{1}{\{1 + 2k_{exp}[\mathrm{PAIA}]_T(0)t\}} \qquad (12)$$

Table 1 Second-order rate constant, k_{exp}[a], for the decomposition of peroxyacetimidic acid in the hydrogen peroxide–acetonitrile system as a function of pH

pH	k_{exp}[b]/dm^3 mol^{-1} s^{-1}	k_{exp}[c]/dm^3 mol^{-1} s^{-1}
9.1	2.2×10^{-5}	3.7×10^{-5}
9.3	2.2×10^{-5}	3.6×10^{-5}
9.9	5.2×10^{-5}	7.8×10^{-5}
10.5	2.6×10^{-4}	1.5×10^{-4}
11.0	2.9×10^{-4}	2.1×10^{-4}
12.0	1.4×10^{-4}	1.3×10^{-4}

[a] $T = 30$ °C. [b] $[CH_3CN](0) = [H_2O_2](0) = 0.94$ mol dm^{-3}. [c] $[CH_3CN](0) = 0.5$ mol dm^{-3}, $[H_2O_2](0) = 5.0$ mol dm^{-3}.

Conversion of eqn. (12) yields eqn. (13) which describes the observation that the plot of $(I_p(t)/\mathrm{mV})^{-1/2}$ *versus* time results in a straight line (see Figs. 1–3). From the slope (sl) and the intercept (int) the second-order rate constant k_{exp} can be estimated.

$$\frac{1}{\sqrt{I_p(t)}} = \frac{1}{\sqrt{Ck_{exp}}[\mathrm{PAIA}]_T(0)} + \frac{2k_{exp}t}{\sqrt{Ck_{exp}}} \quad (13)$$

Alternatively, it is also conceivable that equilibrium (7) is shifted to the side of the educts. It was pointed out by Sauer and Edwards[22] that the constant of formation of 2-hydroxy-2-hydroperoxypropane in the primary addition reaction between hydrogen peroxide and acetone was calculated to be $K_f = 6.4 \times 10^{-2}$ dm^3 mol^{-1} at $T = 32$ °C. However, if the formation constant K_7 of PAIA were of similar magnitude then $K_f^{H_2O_2}$-(acetone), the rate for the formation of $^1O_2$, would show a second-order dependence in the concentration of acetonitrile and hydrogen peroxide. In this case *e.g.* for systems with a large excess of hydrogen peroxide for the rate of $^1O_2$ formation the pseudo-second-order rate law (14) should be valid:

$$\frac{d[^1O_2]}{dt} = -\frac{1}{2}\frac{d[CH_3CN]}{dt} = k'_{exp}[CH_3CN]^2 \quad (14)$$

where k'_{exp} is defined by eqn. (15):

$$k'_{exp} = K_7^2 k_8 F_H [H_2O_2]^2(0) \quad (15)$$

According to eqn. (15) the pseudo-second-order rate constant k'_{exp} should be proportional to the square of the concentration of hydrogen peroxide. Thus at a given pH and a given concentration of acetonitrile the rate of $^1O_2$ formation and as a consequence the value of the phosphorescence intensity, $I_p(0)$, should considerably increase with increasing excess of hydrogen peroxide. However, this is not observed. Our results are only consistent with the assumption that equilibrium (7) is practically shifted to PAIA, *i.e.* K_7 must be several orders of magnitude higher than $K_f^{H_2O_2}$(acetone).

A.4 Second-order rate constant k_{exp} as a function of pH. The values of k_{exp} were determined with either equimolar quantities of hydrogen peroxide and acetonitrile or with a tenfold excess of hydrogen peroxide at $T = 30$ °C in the pH range $9.1 < \mathrm{pH} < 12.0$ and are summarized in Table 1.

The values displayed are mean values calculated from at least three different measurements. The error of k_{exp} amounts to about 25%. The considerable error results mainly from the fact that the $^1O_2$ phosphorescence intensity detected under the used conditions is relatively low (see the signal/noise ratio of the $I_p(t)$ curves in Figs. 1 and 2).

Some experiments were also performed with systems containing a tenfold excess of acetonitrile ($[CH_3CN] = 5.0$ mol dm^{-3}). For these systems values of k_{exp} were observed at a given pH which are generally by a factor of about 4 higher than the corresponding values of Table 1. In addition the $^1O_2$ phosphorescence intensity $I_p(0)$ is generally found to be higher at a given pH than that observed for the system with a tenfold excess of hydrogen peroxide ($[H_2O_2] = 5.0$ mol dm^{-3}). Obviously solvent effects give rise to both results. Water solution containing 5.0 mol dm^{-3} of acetonitrile represents a 26% acetonitrile solution. In such a solution both the constant k_p and the lifetime τ_Δ increase compared to water. With the values of $k_p(\mathrm{water}) = 0.21$ s^{-1}, $k_p(\mathrm{acetonitrile}) = 0.44$ s^{-1},[15] $\tau_\Delta(\mathrm{water}) = 3.1$ µs and $\tau_\Delta(\mathrm{acetonitrile}) = 75$ µs[15] valid at $T = 25$ °C and the molarities of water and acetonitrile, respectively, the values of $k_p(26\%\ CH_3CN) = 0.27$ s^{-1} and $\tau_\Delta(26\%\ CH_3CN) = 4.1$ µs can be estimated.[15] The increase of k_p and τ_Δ is accompanied by an increase of $I_p(0)$ according to eqn. (4). Furthermore in a 26% acetonitrile solution most probably the solvation, especially of PAIA$^-$-anion, is not as strong as in water and consequently the nucleophilic attack of the PAIA$^-$-anion either at the carbon atom of the >C=NH group of PAIA or at the outer peroxide oxygen of PAIA occurs faster than in pure water.

Inspection of Table 1 reveals that the values of k_{exp} determined under different conditions agree very well within the error as mentioned above. In accordance with the mechanism postulated in Scheme 2 the values of k_{exp} run through a maximum with increasing pH. The maximum of the pH–rate profile (Fig. 5) is reached at about pH 11 indicating that the pK_a value of PAIA should amount to about 11. The experimental data (k_{exp}) can be well reproduced by assuming $K_a(\mathrm{PAIA}) = 8 \times 10^{-12}$ mol dm^{-3} and $k_8 = 1.2 \times 10^{-3}$ dm^3 mol^{-1} s^{-1} for the second-order rate constant for the self-decomposition of peroxyacetimidic acid (see Fig. 5).

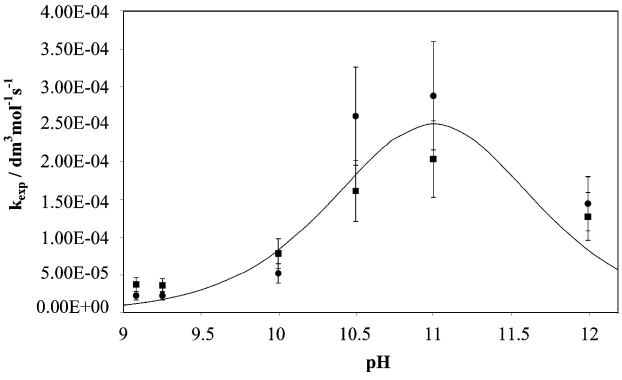


Fig. 5 Calculated rate constants, k_{calc}, represented by the curve (estimated with $k_8 = 1.2 \times 10^{-3}$ dm^{-3} mol^{-1} s^{-1} and $K_a(\mathrm{PAIA}) = 8 \times 10^{-12}$ mol dm^{-3}) and the experimental rate constants, k_{exp}, as a function of pH. The circles represent the k_{exp}-values of the second column of Table 1, the squares denote the k_{exp}-values of the third column.

It is obvious that the rate constant k_8(PAIA) for the heterolytic self-decomposition of PAIA is of the same order as the corresponding rate constant observed for the decomposition of peroxyacetic acid (PAA) by Evans and Upton[23] [$k_8(\mathrm{PAA}) = 2.0 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}] as well as the rate-constant of PAA determind by Koubek *et al.*[19a] [$k_8(\mathrm{PAA}) = 5.4 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}].

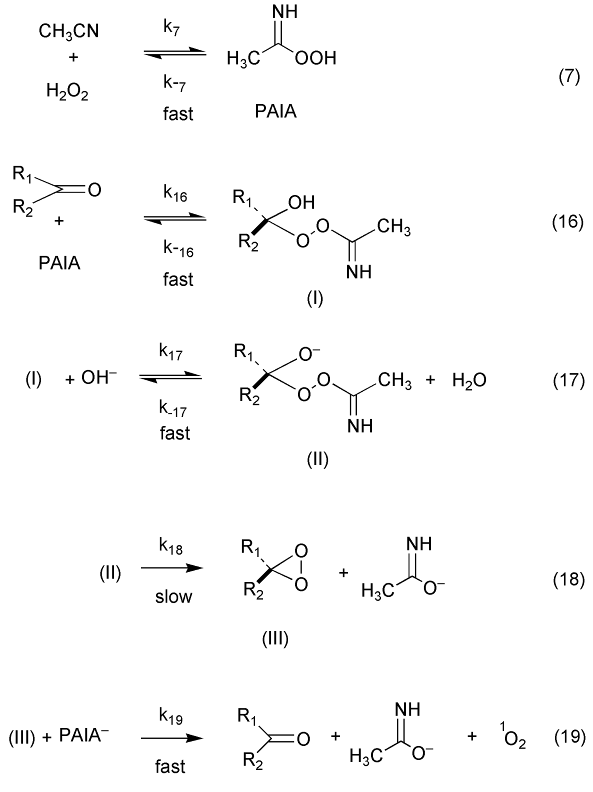
Although there is a remarkably similar geometry of peroxycarboxylic acids and peroxycarboximidic acids[24] we conclude that PAA is the more reactive epoxidizing agent as compared to PAIA. However, PAIA has a significantly higher pK_a value (11.1) than PAA [pK_a(PAA) = 8.2]. Thus PAIA can be used as an epoxidation agent up to about pH 8.5, whereas using PAA at pH ~ 8.5 the self-decomposition of PAA strongly competes with the epoxidation reactions.

The pK_a(PAIA) value of peroxyacetimidic acid is comparable with the pK_a values of hydroperoxides,[25] *e.g.* of H_2O_2 (pK_a = 11.75), of CH_3OOH (pK_a = 11.08) and of C_2H_5OOH

(pK_a = 11.05). But, most probably within the peroxycarboximidic acids PAIA is no exception. From bleaching experiments on tea using PAA generated by the reaction of tetraacetylethylenediamine with hydrogen peroxide it is well known that the bleaching power runs through a maximum with increasing pH.[26] The maximum bleaching effect is found at pH = pK_a(PAA) = 8.2. Recently Reinhardt and Löffler[27] have investigated the bleaching of tea stain as a function of pH using the *N*,*N*-dimethylmorpholiniumacetonitrile–H_2O_2 system and the cyanopyrrolidine–H_2O_2 system. For the first system the maximum bleaching effect was found to be at pH 9.5 and for the second system at pH 11.0, respectively.

B. Investigation of the CH_3CN–H_2O_2 sytem in water in the presence of ketones

As discussed in section A the decomposition of PAIA occurs *via* a mechanism generally observed for peroxy acids. Thus by analogy with the ketone-catalysed decomposition of peroxy acids[8,9] the mechanism presented in Scheme 3 can be postulated



Scheme 3

also for the ketone-catalysed decomposition of PAIA and in general for peroxycarboximidic acids. For simplification the hydration equilibrium between the ketone and its *gem* H_2O-adduct[8g] and additionally the perhydration equilibrium between the ketone and its *gem* H_2O_2-adduct were not taken into account. Furthermore, the dissociation equilibria of the different adducts were neglected (*vide infra*).

Analogous to the peroxy acids, PAIA is assumed to react very fast with the ketone to form the adduct I, *i.e.* the successive reaction of PAIA is not the rate-determining step as observed for the uncatalysed reaction of acetonitrile with hydrogen peroxide. According to Scheme 3 eqn. (20) can be derived for the rate of $^1O_2$ formation.

$$\frac{d[^1O_2]}{dt} = -\frac{1}{2}\frac{d[CH_3CN]}{dt} = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = k_{obs}[CH_3CN][H_2O_2] \qquad (20)$$

where k_{obs} is given by eqn. (21):

$$k_{obs} = K_7 K_{16} K_{17} k_{18} F'_H\,[\text{ketone}](0) \qquad (21)$$

K_7, K_{16} and K_{17} are the constants of the equilibria (7), (16) and (17) and k_{18} denotes the first-order rate constant of the rate-determining step for the formation of the reactive dioxirane III from the intermediate II. The factor F'_H is a constant at a given pH and is defined by eqn. (22).

$$F'_H = \frac{K_w}{\{[H^+] + K_a(\text{PAIA})\}} \qquad (22)$$

Here K_W is the ionic product of water. Finally, [ketone](0) represents the initial concentration of the ketone at starting time.

Interestingly, eqn. (20) is consistent with the observation made by Wiberg[2] for the reaction between benzonitrile derivatives and hydrogen peroxide in 25–50% acetone solutions. According to eqn. (20) the rate of consumption of hydrogen peroxide should show a first-order dependence in [R–CN] and in [H_2O_2]. However, this rate does not show a first-order in OH^- concentration, but is directly proportional to the factor F'_H, as demonstrated for the ketone-catalysed decomposition of Caro's acid.[8f]

To test whether ketones catalysed the reaction of acetonitrile with hydrogen peroxide we have performed an experiment with $DMOP^+$ NO_3^-. Taking into account the electron-withdrawing ammonium group of $DMOP^+$ NO_3^- it is one of the most reactive catalysts in the ketone-catalysed decomposition of peroxy acids and has been shown to display a dramatic acceleration of peroxy acid decomposition.[8a,8f,8g,11]

Inspection of the $I_p(t)$ curve presented in Fig. 6 clearly demonstrates the influence of $DMOP^+$ NO_3^- in the reaction of acetonitrile with hydrogen peroxide. As shown in curve a in comparison with curve b, the addition of a small amount of $DMOP^+$ NO_3^- to a system containing equimolar quantities of the educts leads to a considerable increase of $I_p(t)$. This may be explained as a consequence of an enhancement of the decomposition of PAIA.

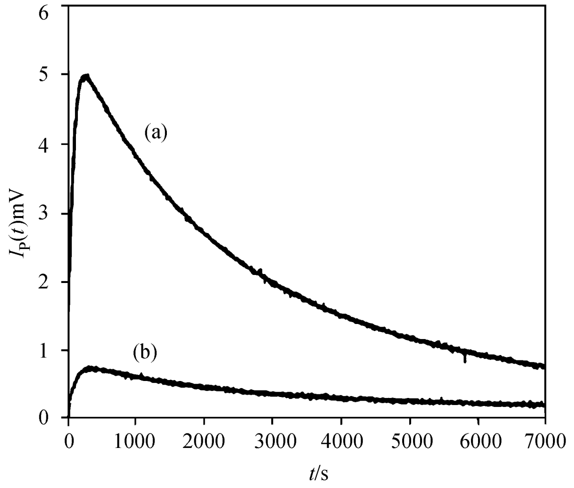


Fig. 6 $I_p(t)$ as a function of time for the reaction between acetonitrile and hydrogen peroxide in the presence of $DMOP^+$ NO_3^- (curve a) and in the absence of $DMOP^+$ NO_3^- (curve b). Conditions: [CH_3CN](0) = [H_2O_2](0) = 0.94 mol dm^{-3}; [Dequest] = 1.0 × 10^{-4} mol dm^{-3}, pH = 9.5, T = 30 °C and [$DMOP^+$ NO_3^-] = 5.0 × 10^{-2} mol dm^{-3}.

According to eqn. (20) one can expect that the difference $\Delta I_p(t) = I_p(t)$ [curve a] − $I_p(t)$ [curve b] can be described by a second-order plot $(\Delta I_p(t)/\text{mV})^{-1/2}$ *versus* time. However, such a plot does not yield a straight line over the whole reaction time

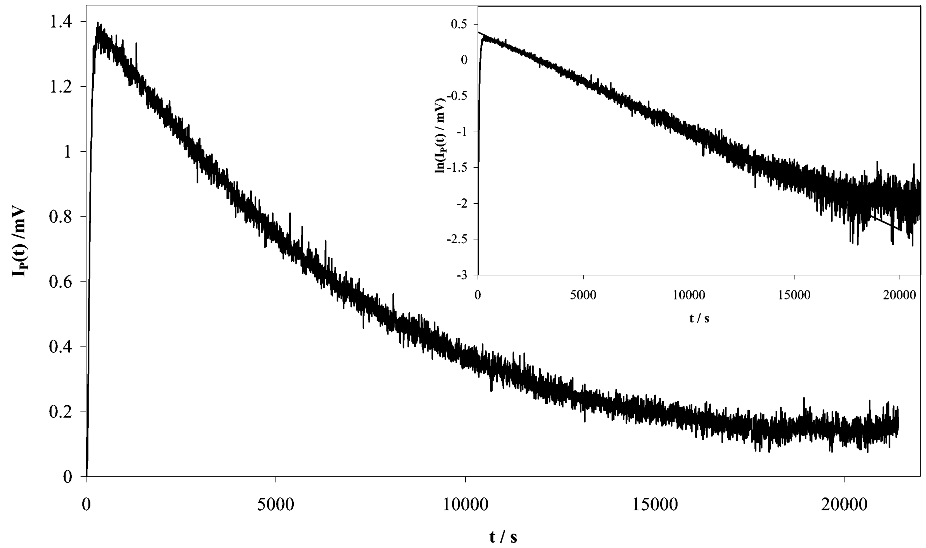


Fig. 7 $I_p(t)$ as a function of time for the reaction between acetonitrile and hydrogen peroxide in 50% acetone solution. Conditions: $[CH_3CN](0) = 0.1$ mol dm^{-3}, $[H_2O_2](0) = 1.0$ mol dm^{-3}, [Dequest] = 1.0×10^{-4} mol dm^{-3}, pH = 8.2 and $T = 60$ °C. The inset shows the corresponding plot of ln ($I_p(t)$/mV) *versus* time; (sl = 1.4×10^{-4} s^{-1}).

indicating that the DMOP$^+$ NO_3^--catalysed decomposition of PAIA is more complex than the mechanism given in Scheme 3 predicts. Obviously for DMOP$^+$ NO_3^- the hydration equilibrium and the perhydration equilibrium, respectively, between DMOP$^+$ NO_3^- and the corresponding adducts must be taken into account.

To further illustrate the dioxirane formation in the acetonitrile–hydrogen peroxide–ketone system we used acetone as catalyst. In contrast to DMOP$^+$ NO_3^- the simplified mechanism should be valid using acetone as catalyst, since the formation constant $K_f^{H_2O}$(acetone) for the H_2O-adduct and the formation constant $K_f^{H_2O_2}$(acetone) for the H_2O_2-adduct are sufficiently small that the corresponding equilibria can be neglected. However, high concentrations of acetone are necessary to demonstrate the influence of acetone as catalyst in the hydrogen peroxide–acetonitrile system because acetone is by a factor of about 1000 (pH ≤ 9) less efficient as catalyst than DMOP$^+$ NO_3^-.[8f,8g] To avoid a contribution of the uncatalysed reaction we have performed measurements at pH 8.2 and $T = 60$ °C with a tenfold excess of hydrogen peroxide ($[H_2O_2] = 1.0$ mol dm^{-3}) in 50% acetone. Accordingly, no $^1O_2$ was detected under the same conditions only with the hydrogen peroxide–acetonitrile system itself in the absence of acetone. Fig. 7 shows that eqn. (20) describes the acetone-catalysed decomposition of PAIA. If a large excess of hydrogen peroxide is used eqn. (20) yields for the time dependence of $I_p(t)$ eqn. (23).

$$I_p(t) = I_p(0)e^{-2k'_{obs}t} \qquad (23)$$

where $I_p(0)$ is defined by eqn. (24)

$$I_p(0) = C'k'_{obs}\,[CH_3CN](0) \qquad (24)$$

Here k'_{obs} is given by eqn. (25)

$$k'_{obs} = k_{obs}\,[H_2O_2](0) \qquad (25)$$

and C' represents the product of ck_p(50% acetone)τ_Δ(50% acetone).

According to eqn. (23) the pseudo-first-order plot of ln ($I_p(t)$/mV) *versus* time resulted in a straight line up to 14000 s as shown in the inset of Fig. 7. From the slope of the straight line $2k'_{obs}$ is determined to be 1.4×10^{-4} s^{-1}. Consequently the pseudo-first-order plot is linear through three half-lives. For k_{obs} a value of $k_{obs} = K_7\,K_{16}\,K_{17}\,k_{18}\,F'_H$[acetone](0) = 7.0×10^{-5} dm^3 mol^{-1} s^{-1} can be estimated. With $F'_H = 1.7 \times 10^{-6}$ mol dm^3 at pH 8.2 and with [acetone](0) = 6.8 mol dm^{-3} the fourth-order rate constant, k_{Di}, for the formation of dimethyldioxirane is calculated to be $k_{Di} = K_7\,K_{16}\,K_{17}\,k_{18} = 6.1$ (dm^3 mol^{-1})^3 s^{-1}.

The formation of a dioxirane in the acetonitrile–hydrogen peroxide–ketone system is in agreement with the recent study of Shu and Shi[6] who demonstrated the efficient epoxidation of olefins using CH_3CN–H_2O_2 and different ketones as catalyst. It was found that trifluoroacetone (CF_3COCH_3) as catalyst gave the highest conversion in a 1 : 1 mixture of CH_3CN and aqueous EDTA solution using *trans*-β-methylstyrene as substrate, whereas in the absence of ketone catalyst, the epoxidation was minimal under the same conditions. Interestingly, upon the determination of the optimal reaction pH, the best epoxide conversion was found to be at pH around 11, *i.e.* at the pK_a value of PAIA.[28] This result seems to be no exception. Shu and Shi[6] have also investigated the epoxidation of *trans*-β-methylstyrene as substrate using the Caro's acid–CF_3COCH_3 system as a function of pH. Obviously the pH has a large effect on the epoxidation and a maximum conversion of the substrate was observed at pH 10, *i.e.* also around the pK_{a2} value of the monoanion of Caro's acid (HSO_5^-) with pK_{a2} = 9.4.

For a more detailed study of the ketone-catalysed decomposition of peroxycarboximidic acids (PCIA) a water soluble nitrile–H_2O_2 system should be used generating a more reactive PCIA than PAIA. For example, with a nitrile quat like *N*-methylmorpholiniumacetonitrile[29] it should be possible to measure the ketone-catalysed decomposition of the PMIA$^+$-cation with relatively small concentrations of ketones like acetone, cyclohexanone and fluoroacetone, *i.e.* with concentrations of the ketones which are not accompanied by a remarkable change in the properties of the solvent.

Conclusions

Our results indicate that peroxyacetimidic acid (PAIA) does not react with hydrogen peroxide to form acetamide and $^1O_2$. This is true for both the uncatalysed and the ketone-catalysed decomposition of PAIA. The observation that even the reaction of PAIA with the HOO$^-$ anion can obviously not compete with the reaction of PAIA and the PAIA$^-$-anion indicates that PAIA$^-$ is more nucleophilic than HOO$^-$.

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28 It is worthy of note here that the uncatalysed decomposition of peroxyacetimic acid with maximum rate at pH = pK_a = 11.1 forming quantitatively singlet oxygen can be neglected in the acetonitrile–hydrogen peroxide system catalysed by trifluoroacetone due to the slow rate constant of the uncatalysed self-decomposition.

29 The nitrile quat with hydrogensulfate as counterion was until recently commercially available under the trade name Sokalan® BM G from BASF AG.