Activation of hydrogen peroxide by *p*-nitrophenyl chloroformate. Indication for *in situ* formation of carbon trioxide and evidence for singlet oxygen generation by the chloride-catalysed decomposition of hydrogen peroxide in acidic solution

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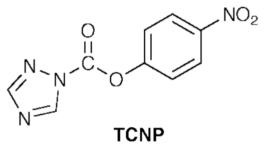
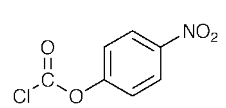
The kinetics of the activation of hydrogen peroxide by *p*-nitrophenyl chloroformate (NPCF) in tetrahydrofuran (THF) have been investigated by measuring the phosphorescence of the released singlet molecular oxygen ($^1O_2$) at 1270 nm. The results are consistent with the assumption that the reaction between hydrogen peroxide and NPCF under pseudo first-order conditions with respect to hydrogen peroxide proceeds *via* a consecutive, pseudo first-order reaction. In the first pseudo first-order reaction *O*-*p*-nitrophenyl monoperoxycarbonic acid **1** and hydrochloric acid are formed. The corresponding second-order rate constant at $T = 20$ °C was found to be $k_5 = (2.6 \pm 0.5) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}. In the second pseudo first-order reaction **1** undergoes an acid-catalysed decomposition to give, in the end, besides *p*-nitrophenol, carbon trioxide (CO_3), the anhydride of the unstable monoperoxycarbonic acid. The pseudo first-order rate constant of this catalysis was determined to be $k_{10} = (2.9 \pm 0.4) \times 10^{-3}$ s^{-1} at $T = 20$ °C. The Arrhenius parameters determined for both reactions are consistent with the assumption that the formation of **1** occurs according to a $B_{AC}2$-mechanism and that the acid-catalysed decomposition of **1** occurs according to an $A_{AC}1$-mechanism. The assumption that **1** in the NPCF–H_2O_2 system undergoes an acid-catalysed decomposition to give CO_3 is confirmed by the results of the measurements carried out with the 1*H*-1,2,4-triazolecarboxylic acid *p*-nitrophenyl ester (TCNP)–H_2O_2 system in THF in the presence of sulfuric acid. Moreover, in the NPCF–H_2O_2–THF system $^1O_2$ is generated by the decomposition of hydrogen peroxide catalysed by chloride. The fact that in acidic solution $^1O_2$ is formed by a chloride-catalysed decomposition of hydrogen peroxide is confirmed by measurements carried out with hydrochloric acid–H_2O_2 systems in THF and in water, respectively. For the latter system it is found that the oxygen liberated is exclusively formed as $^1O_2$.

Introduction

Very recently we have reported on the nucleophilic activation of hydrogen peroxide by 1*H*-1,2,4-triazolecarboxylic acid *p*-nitrophenyl ester (TCNP).[1] This compound reacts in tetrahydrofuran (THF) with 30% hydrogen peroxide *via* a competitive, consecutive second-order reaction to give one mole of singlet oxygen ($^1O_2$) per mole of TCNP. In the first reaction *O*-*p*-nitrophenyl monoperoxycarbonic acid (**1**) is generated which further reacts with hydrogen peroxide to give, in the end, $^1O_2$. **1** is a very reactive peroxy acid, *e.g.*, it is, by a factor of about 100, more reactive towards cyclohexene than peroxybenzoic acid.[1]



TCNP



NPCF

O-Aryl (alkyl) monoperoxycarbonic acids are of interest for the following reasons. i) They are powerful oxygenating agents.[1–3] ii) They have the advantage that oxygen transfer from these peroxy acids to a substrate is connected with the generation of the corresponding monoester of the carbonic acid, which quickly decomposes to give carbon dioxide, the corresponding phenol and alcohol, respectively. In contrast to conventional carboxylic acids no strong parent acids are formed, thus no substantial pH changes take place. iii) Finally, *O*-aryl (alkyl) monoperoxycarbonic acids can be regarded as sources for the *in situ* formation of the monoperoxycarbonic acid (H_2CO_4).

To prove the assumption that H_2CO_4 could be formed by acid-catalysed cleavage of the ester bond we have performed measurements with *p*-nitrophenyl chloroformate. In this system **1** should be generated as an intermediate besides hydrochloric acid. In addition measurements were carried out with the TCNP–H_2O_2 system in the presence of sulfuric acid.

Experimental

Materials

p-Nitrophenyl chloroformate (NPCF) (purum ≥ 97%), (*E*)-stilbene ((*E*)-1,2-diphenylethylene (purum ≈ 97%)), *trans*-1,2-diphenyloxirane (purum ≥ 98%), cyclohexene (puriss. p.a.) and THF (for HPLC) were purchased from Fluka and used as received. 1*H*-1,2,4-Triazolecarboxylic acid *p*-nitrophenyl ester (TCNP) was synthesized as described.[1] 30% Hydrogen peroxide (pract.) came from Merck. Sulfuric acid (Konzentrat für Maßlösung 1 N), hydrochloric acid (Konzentrat für Maßlösung 1N) and sodium bromide (p.a.) from Fluka were used as received. For the preparation of the acid solutions twice distilled water was used. Dequest 2066 (Monsanto), an effective metal-chelating agent, was kindly donated by Clariant GmbH, Frankfurt am Main/Höchst. Cerium(IV) sulfate standard solution came from Riedel-de Haën.

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Experimental procedures

a. Determination of hydrogen peroxide concentration. The concentration of hydrogen peroxide was determined by titrating samples of 200 µL taken from the reaction mixture with a cerium(IV) sulfate standard solution using ferroin solution as redox indicator.[4]

b. Gas-volumetric measurements. The gas-volumetric measurements were performed according to the procedure described by Rebek *et al.*[5] We have measured the gases evolved in the reaction between NPCF and twice-distilled water and in addition between NPCF and 30% hydrogen peroxide both in the absence and the presence of cyclohexene.

c. Singlet oxygen infrared emission measurements. The near infrared luminescence (IRL)-spectrometer used in our studies for recording the $^1O_2$-phosphorescence at $\lambda = 1270$ nm has been described in detail.[6–9] For the intensity of the $^1O_2$ phosphorescence emission, I_P, eqn. (1) holds,[8] where c (1.4×10^{11} mV dm^3 mol^{-1} s) is a constant of the IRL-spectrometer, k_p is the rate constant of the $^1O_2$-phosphorescence emission, τ_Δ is the lifetime of $^1O_2$ and d[$^1O_2$]/dt denotes the rate of $^1O_2$ formation. Both k_p and τ_Δ depend on the solvent and solvent mixture, respectively.[1] The values of k_p and τ_Δ used for the calculation of d[$^1O_2$]/dt and for the concentration of [$^1O_2$] are: i) for the NPCF–H_2O_2 system in THF: $k_p = 0.45$ s^{-1} and $\tau_\Delta = 18$ µs (ref. 1); ii) for aqueous solutions: $k_p = 0.18$ s^{-1} (ref. 8) and $\tau_\Delta = 3.1$ µs (ref. 10).

$$I_P(t) = ck_p\tau_\Delta \frac{d[^1O_2]}{dt} \qquad (1)$$

The concentration of $^1O_2$ can be calculated according to eqn. (2), were C represents the product $ck_p\tau_\Delta$.

$$[^1O_2] = \frac{1}{C}\int_{t=0}^{t} I_P(t)dt \qquad (2)$$

d. Reaction procedure. Reactions were carried out in thermostatted 1 cm quartz cuvettes. To the THF solutions of NPCF, TCNP + H_2SO_4 and TCNP + (*E*)-stilbene, for example, 30% hydrogen peroxide was added by a micro syringe. Vigorous stirring was necessary. The initial concentrations of the reactants used are given in the legends of the figures or in the text.

Results and discussion

A. $^1O_2$ phosphorescence intensity $I_P(t)$ as a function of time of the *p*-nitrophenyl chloroformate (NPCF)–H_2O_2 system in THF

Fig. 1 shows a plot of $I_P(t)$ *versus* time obtained for the NPCF–H_2O_2 system in THF under pseudo first-order conditions with respect to hydrogen peroxide at $T = 20$ °C. After addition of hydrogen peroxide to the NPCF solution an induction period of about 40 s is observed. After this time $I_P(t)$ increases considerably, reaches a maximum at $t = 218$ s and then decreases exponentially, but only for a short time until $t = 630$ s as demonstrated by the plot of ln $I_P(t)$ *versus* time depicted in the inset of Fig. 1. After $t = 630$ s $I_P(t)$ decreases more slowly compared to the exponential decrease (see the dotted curve a) and reaches, at $t \geq 1750$ s (see curve b), a constant value of $I_P(t) = 5$ mV indicating that the rate of $^1O_2$ formation is constant. Under the conditions used the constant rate was observed over a period of one hour. This very surprising result can be explained by the assumption that the $^1O_2$ observed at $t > 1750$ s is generated by a chloride-catalysed decomposition of hydrogen peroxide in the acidic solution (*vide infra*).

The course of the $I_P(t)$ curve between $t = 45$ and 630 s comes close to that observed under pseudo first-order conditions with respect to hydrogen peroxide for the TCNP–H_2O_2 system.[1] Thus it can be assumed that during this time the precursor of $^1O_2$ is formed *via* a sequence of two pseudo first-order reactions. Under such conditions eqn. (3) can be derived,[1] where [NPCF]$_0$ is the initial concentration of NPCF, k_f' denotes the pseudo first-order rate constant of the fast reaction and k_s' the pseudo first-order rate constant of the slow reaction, respectively[1] and η represents the efficiency of the $^1O_2$-formation. k_s' can be evaluated from the plot of $I_P(t)$ *versus* time, which yields, at longer times, a straight line (see the inset of Fig. 1) with the slope equal to $-k_s'$. The rate constant of the faster reaction can be calculated from t_{max}, *i.e.* from the time at which $I_P(t)$ exhibits its maximum. t_{max} is defined by eqn. (4).

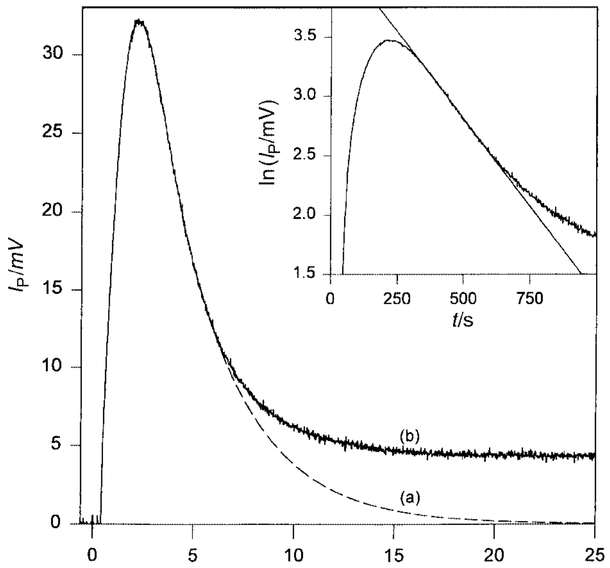
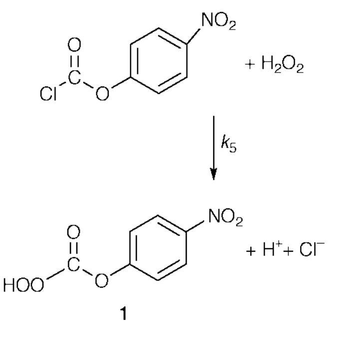


Fig. 1 $I_P(t)$ as a function of time for the system NPCF–H_2O_2 in THF. The inset shows the corresponding plot of ln $I_P(t)$ *versus* time between 0 and 1000 s. Conditions: [NPCF] = 2.64×10^{-2} mol dm^{-3}; [H_2O_2] = 2.64×10^{-1} mol dm^{-3}; $T = 20$ °C.

$$I_P(t) = \eta Ck_s'[\text{NPCF}]_0 \frac{k_f'}{k_s' - k_f'} \{\exp(-k_f't) - \exp(-k_s't)\} \qquad (3)$$

$$t_{max} = \frac{1}{k_s' - k_f'} \ln\left(\frac{k_s'}{k_f'}\right) \qquad (4)$$

The pseudo first-order rate constants were found to be as follows at $T = 20$ °C: k_f'(NPCF) = $(6.8 \pm 1.4) \times 10^{-3}$ s^{-1}; k_s'(NPCF) = $(2.9 \pm 0.4) \times 10^{-3}$ s^{-1}. By analogy with the TCNP–H_2O_2 system[1] in the first reaction (5) of the NPCF-system the reactive *O*-*p*-nitrophenyl monoperoxycarbonic acid (**1**) should also be formed.



(5)

Eqns. (3) and (4) alone cannot tell us which of the rate constants correlate with reaction (5). To determine which, the

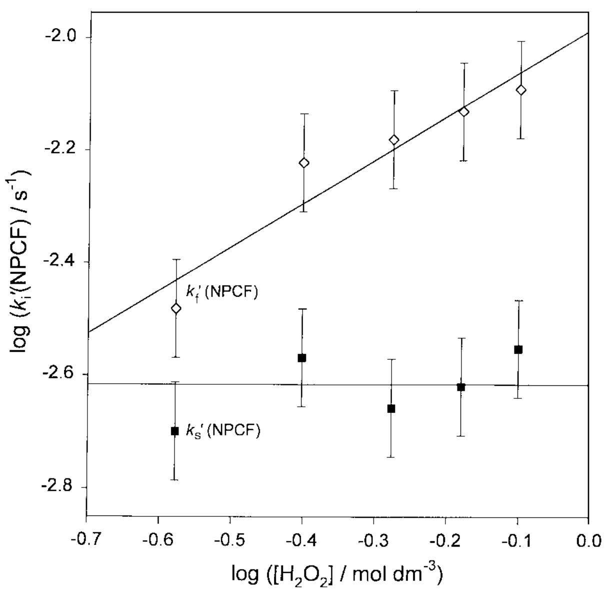


Fig. 2 Double logarithmic plots of k_i'(NPCF) *versus* [H_2O_2] for the NPCF–H_2O_2 system in THF. Conditions: [NPCF] = 2.64 × 10^{-2} mol dm^{-1}; T = 15 °C.

amount of $^1O_2$ evolved in the two reactions must be known and further kinetic measurements are necessary.

The area under curve a (see Fig. 1) corresponds to the amount of $^1O_2$ expected for the NPCF–H_2O_2 system if the chloride-catalysed decomposition of hydrogen peroxide doesn't take place. The area was estimated to be (16705 ± 4%) mVs and according to eqn. (2) with $k_p = 0.45$ s^{-1} and $\tau_\Delta = 18.0$ µs (ref. 1) for the concentration of $^1O_2$ a value of [$^1O_2$] = 1.5 × 10^{-2} mol dm^{-3} is obtained. From this value and the initial concentration $[NPCF]_0$ = 2.64 × 10^{-2} mol dm^{-3} used in this experiment, it follows that the efficiency $\eta = [^1O_2]/[NPCF]_0$ amounts to about 0.6. This value indicates that in the NPCF–H_2O_2 system, neglecting the chloride-catalysed decomposition of hydrogen peroxide, in contrast to the TCNP–H_2O_2 system, only about $\frac{1}{2}$ mol of $^1O_2$ is generated from 1 mol of NPCF.

In agreement with this observation are the results of the gas-volumetric measurements carried out in THF with the NPCF–H_2O_2 system in comparison to the NPCF–H_2O system. Concentrations of NPCF between 7.6 × 10^{-4} and 1.9 × 10^{-3} were used and in the experiments with hydrogen peroxide a concentration of [H_2O_2] = 2.2 × 10^{-2} mol dm^{-3} was employed. The end of gas evolution caused by the two reactions was determined using the velocity of gas liberation. For example, for a NPCF–H_2O_2 system, under conditions comparable with those used in the attempt described in Fig. 1, the volume of gas measured at 1100 s was used for the calculation: independently of the ratio of [NPCF]/[H_2O_2] employed it was found that 1.6 ± 0.1 mol of gas is generated from 1 mol of NPCF. Moreover, in the presence of an excess of cyclohexene, only 1 mol of gas is liberated. These results are in excellent agreement with the result obtained by the $I_P(t)$ measurements indicating that only $\frac{1}{2}$ mol of $^1O_2$ is generated from 1 mol of NPCF.

Considering this result it can be deduced that hydrogen peroxide can only be involved in one of the two reactions. Obviously this should be the case for the first of both reactions.

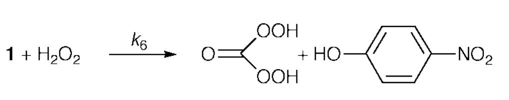
B. $I_P(t)$ measurements as a function of the concentration of hydrogen peroxide

Measurements at a given concentration of NPCF as a function of the concentration of hydrogen peroxide were carried out, to clarify whether k_f'(NPCF) or k_s'(NPCF) depends on the concentration of hydrogen peroxide. The results are presented in Fig. 2. It is seen that k_f'(NPCF) strongly depends on the concentration of hydrogen peroxide. The slope of the straight line of the double logarithmic plot of k_f'(NPCF) *versus* [H_2O_2] amounts to about 0.90 ± 0.10 indicating that, within the error limits, k_f'(NPCF) is of first-order with respect to hydrogen peroxide. In contrast k_s'(NPCF) is found to be actually independent of [H_2O_2].

This result indicates that k_f'(NPCF) correlates with reaction (5) and moreover that reaction (5) occurs faster than the consecutive reaction (see on). At this stage the second-order rate constant $k_5 = k_f(NPCF) = k_f'(NPCF)/[H_2O_2]$ = 2.6 × 10^{-2} dm^3 mol^{-1} s^{-1} observed at T = 20 °C in the NPCF–H_2O_2 system should be compared with the second-order rate constant k_f(TCNP) = 1.1 × 10^{-3} dm^3 mol^{-1} s^{-1} at T = 20 °C.[1] It can be seen that k_f(NPCF) is, by a factor of about 25, greater than k_f(TCNP). This result is in agreement with the fact that in the NPCF–H_2O_2 system, in the first reaction hydrochloric acid is eliminated. Since chloride ion is less basic than the 1,2,4-triazole eliminated in the first reaction of the TCNP–H_2O_2 system,[1] chloride ion should be the better leaving group and consequently its elimination should occur faster than that of 1,2,4-triazole.

C. $I_P(t)$ measurements as a function of the concentration of *p*-nitrophenyl chloroformate (NPCF)

In the TCNP–H_2O_2 system **1** further reacts with hydrogen peroxide according to eqn. (6) to give, most probably, diper-



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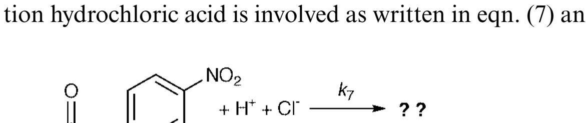
(6)

oxycarbonic acid **2**,[1,5] which may be the precursor of $^1O_2$ in this system. However, in the NPCF–H_2O_2 system reaction (6) doesn't take place. This conclusion can be drawn solely by comparing the rate constants of the slower reactions determined for the different systems. For a concentration of hydrogen peroxide of about [H_2O_2] = 2.64 × 10^{-1} mol dm^{-3} (see legend of Fig. 1) for the pseudo first-order rate constant k_s'(TCNP) at T = 20 °C a value of 1.9 × 10^{-4} s^{-1} can be estimated,[1] whereas k_s'(NPCF) is found to be 2.9 × 10^{-3} s^{-1} (*vide supra*). Thus k_s'(NPCF) is, by a factor of about 15, greater than k_s'(TCNP).

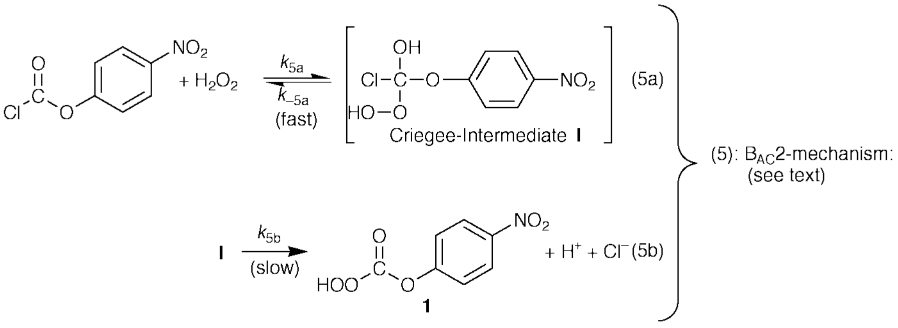
In reaction (5), besides **1**, hydrochloric acid is generated and obviously this is the reason that in the NPCF–H_2O_2 system reaction (6) does not take place, *i.e.* that the mechanism of $^1O_2$ formation differs from that observed in the TCNP–H_2O_2 system.

It seems reasonable that in the second, slower first-order reaction hydrochloric acid is involved as written in eqn. (7) and as a



(7)

consequence k_s'(NPCF) is connected with reaction (7). As yet no prediction can be made about the mechanism and therefore about the products generated. To prove whether reaction (7) is working we have performed measurements as a function of the NPCF concentration. The results are given in Fig. 3. It is seen that k_s'(NPCF) strongly depends on the concentration of NPCF, whereas k_f'(NPCF), the pseudo-first order rate constant of the first reaction (5), is independent of [NPCF]. The straight line of the double logarithmic plot of k_s'(NPCF) *versus* [NPCF] with the slope S = 1.0 ± 0.1 indicates that k_s'(NPCF) is first-order with respect to [NPCF] and as a consequence it really depends on the concentration of hydrochloric acid. In this connection it must be noted that we are not aware of the exact concentration of hydrochloric acid, because the first reaction is not completely finished at the time at which k_s'(NPCF) is



Scheme 1

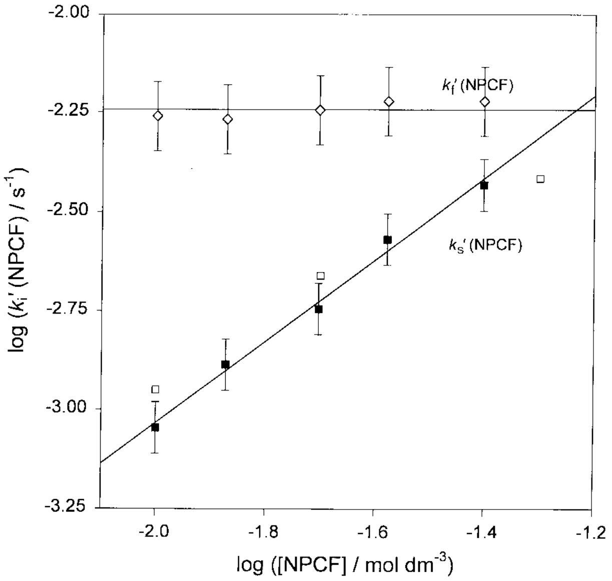


Fig. 3 Double logarithmic plot of k_i'(NPCF) *versus* [NPCF] for the NPCF–H_2O_2 system in THF. Conditions: $[H_2O_2] = 3.96 \times 10^{-1}$ mol dm^{-3}; $T = 15$ °C. For the values denoted by □ see section F.

determined from the slope of the straight line depicted in the inset of Fig. 1. However, from this straight line it can be deduced that reaction (5) has occurred to a great extent, thus the concentration of hydrochloric acid can be regarded as approximately constant.

With respect to the mechanism of the decomposition of **1** generated in the NPCF–H_2O_2 system according to eqn. (7) the following results must be taken into account:

i) The decomposition is independent of the concentration of hydrogen peroxide and since 30% hydrogen peroxide is used, the decomposition of **1** is also independent of the water concentration, and

ii) the decomposition is first-order with respect to the concentration of NPCF.

In principle the following mechanisms for the decomposition of **1** are possible: A. the decomposition catalysed by hydrochloric acid or B. the decomposition *via* an acid-catalysed cleavage of the ester bond.

In connection with these mechanisms the results of the measurements at different temperatures are of interest and should be regarded first.

D. Investigation of the NPCF–H_2O_2 system in THF at different temperatures

The data presented in this section were calculated neglecting the chloride-catalysed decomposition of hydrogen peroxide. The temperature dependence of this reaction will be discussed later.

The measurements as a function of temperature were performed with $[NPCF]_0 = 2.64 \times 10^{-2}$ mol dm^{-3}, $[H_2O_2] = 2.64 \times 10^{-1}$ mol dm^{-3} in THF at five temperatures in the range $5 \le T \le 25$ °C. From the Arrhenius plots of k_f(NPCF) and of $k_s'(\text{NPCF}) = k_7'$, the pseudo-first order rate constant of reaction (7), the following values for the apparent Arrhenius parameters are obtained:

$$\ln A_a(5) = 17 \pm 3;\ E_{aa}(5) = (50 \pm 5)\ \text{kJ mol}^{-1};$$

$$\ln A_a(7) = 14 \pm 2;\ E_{aa}(7) = (49 \pm 5)\ \text{kJ mol}^{-1};$$

As already discussed in the previous paper[1] from the small values of the preexponential factor A_a (here $A_a(5) = 2.4 \times 10^7$ dm^3 mol^{-1} s^{-1} and $A_a(7) = 1.2 \times 10^6$ s^{-1}) it can be deduced that in both reactions a preequilibrium takes place (see Scheme 1 and Scheme 2). As shown in Scheme 1, the formation of the *O*-*p*-nitrophenyl monoperoxycarbonic acid (**1**) should occur *via* the Criegee-intermediate I according to a $B_{AC}2$-mechanism.

E. Mechanism of the decomposition of *O*-*p*-nitrophenyl monoperoxycarbonic acid (1)

E.1. Mechanism A. Since in acidic solutions chloride ions can catalyse the decomposition of hydrogen peroxide,[11–13] whereby $^1O_2$ is generated (*vide infra*) the obvious assumption is that chloride ions can also catalyse the decomposition of peroxycarboxylic acids. And that's why the peroxycarboxylic acids are more powerful oxidants than hydrogen peroxide. Indeed, preliminary tests with *m*-chloroperoxybenzoic acid carried out in HCl (1 N)–THF solutions have unequivocally shown that in this system $^1O_2$ is generated.†

The general rate law of the chloride-catalysed decomposition of hydrogen peroxide is a two term rate law.[12,14] Assuming that a rate law of this type also holds for the chloride-catalysed decomposition of **1** this rate law should have the form given by eqn. (8).

$$-\frac{d[\mathbf{1}]}{dt} = k_7^0[Cl^-][\mathbf{1}] + k_7[H^+][Cl^-][\mathbf{1}] \qquad (8)$$

In acidic solutions the second term in eqn. (8) dominates,[14] *i.e.* k_s'(NPCF) should be equal to $k_7' = k_7[H^+][Cl^-]$. Since in reaction (5) both ions are generated, k_s'(NPCF) should be second-order with respect to the NPCF concentration. However, this is not observed and consequently mechanism A can be excluded.

E.2. Mechanism B. Four mechanisms are discussed for the acid-catalysed ester hydrolysis.[15] Only the $A_{AC}1$-mechanism[15b] is consistent with the results observed. In this mechanism the ester hydrolysis depends on the hydrogen ion concentration and on the ester concentration, but not on the concentration of water. The mechanism postulated for the $^1O_2$ formation *via* an $A_{AC}1$-mechanism for the decomposition of **1** is presented in

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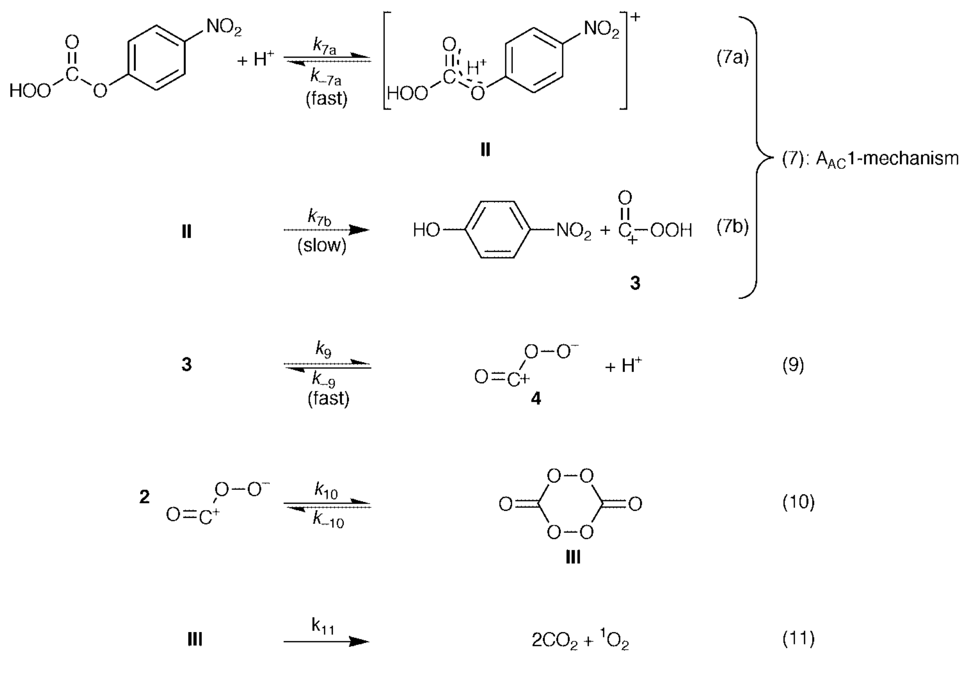
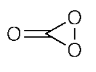
† We intend to investigate this system in more detail and will present the results in a later paper.



Scheme 2 (for formation of **1** see Scheme 1).

Scheme 2. In this mechanism it is assumed, in accordance with the $A_a(7)$ value (*vide supra*) that the acid-catalysed cleavage of the ester bond occurs *via* a preequilibrium between **1** and its protonated form II according to eqn. (7a). II should decompose to give, besides *p*-nitrophenol, the protonated carbon trioxide **3**, *i.e.* the protonated anhydride of the monoperoxycarbonic acid. At first sight it might be expected that **3** will react with hydrogen peroxide to give the diperoxycarbonic acid **2** (see eqn. (6)). But the formation of **2** can be excluded, since in the NPCF–H_2O_2 system, neglecting the generation of $^1O_2$ by the chloride-catalysed decomposition of hydrogen peroxide, only $\frac{1}{2}$ mol of $^1O_2$ is formed. Since hydrogen peroxide is a stronger nucleophile than water the formation of monoperoxycarbonic acid also seems unlikely.

With respect to the monoperoxycarbonic acid, it is well known that only the salts are stable.[16] In water the monoperoxycarbonic acid decomposes rapidly generating, in the end, carbon dioxide and oxygen, whereby most likely carbon trioxide is formed as an intermediate. Up to now the mechanism of the decomposition of carbon trioxide in solution is unknown. In solution carbon trioxide could exist in the dipolar structure (**4**)[17] as described in eqn. (9). It is reasonable to assume that after deprotonation of **3** two molecules of **4** react with one another according to eqn. (10) to give at first the cyclic dimer **III**, which may then decompose to give two molecules of carbon dioxide and one molecule of $^1O_2$. However, it must be noted that after the deprotonation of **3** the cyclic isomer of carbon trioxide **5** could be formed, which should be, according to the theoretical estimation,[18] more stable than the open form **4**.



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The rate law for the reaction of **1** according to eqn. (7) is kinetically expressed by eqn. (12). If reaction (7) is the rate determining step for the $^1O_2$, then $k_s'(\text{NPCF})$ is equal to $k_7' = k_{7a}k_{7b}[H^+]$. k_7' is first-order with respect to $[H^+]$ and therefore first-order with respect to [NPCF]. Thus mechanism B fits the experimental data.

$$-\frac{d[\mathbf{1}]}{dt} = \frac{d[\mathbf{3}]}{dt} = K_{7a}k_{7b}[H^+][\mathbf{1}] \qquad (12)$$

To our best knowledge up to now the $A_{AC}1$-mechanism is only observed in strongly acidic media.[15c] But in the NPCF–H_2O_2 system (see Fig. 1) the maximum hydrogen ion concentration can only reach a value of about 6.2×10^{-2} mol dm^{-3}. Although such a solution is not a strongly acidic media, *a priori* the $A_{AC}1$-mechanism cannot be excluded for the decomposition of **1**.

To clarify whether this mechanism is working in the NPCF–H_2O_2 system, we have carried out measurements with the TCNP–H_2O_2 system in the presence of sulfuric acid.

F. Investigation of the 1*H*-1,2,4-triazolecarboxylic acid *p*-nitrophenyl ester (TCNP)–H_2O_2 system in the presence of hydrogen ions

To investigate the influence of hydrogen ions on the *O*-*p*-nitrophenyl monoperoxycarbonic acid **1** generated in the TCNP–H_2O_2 system, experiments were carried out with this system in THF by adding hydrogen ions as sulfuric acid. Fig. 4 demonstrates the result observed for a system with equal concentrations of TCNP and hydrogen peroxide ($[\text{TCNP}] = [H_2O_2] = 5.2 \times 10^{-2}$ mol dm^{-3}). To this system sulfuric acid ($[H^+] = 2.0 \times 10^{-2}$ mol dm^{-3}) was added after 750 s, *i.e.* at a time at which the original $I_P(t)$ signal has already decreased. After addition of sulfuric acid the $I_P(t)$ signal firstly decreases, most likely due to the decrease of the lifetime τ_Δ of $^1O_2$. But it is evident that after about 830 s the $I_P(t)$ signal increases considerably from about 2 mV up to ≈ 11 mV indicating that the rate of $^1O_2$ formation increases as a result of a change of the mechanism of $^1O_2$ formation.

After about 1130 s the $I_P(t)$ signal decreases according to a pseudo first-order reaction (see the inset of Fig. 4), but not through the whole remaining time of $^1O_2$ formation. This behaviour is also observed for the other experiments. No plausible kinetic explanation of this behaviour can, as yet, be offered.

The pseudo first-order rate constant $k_{H^+}(\text{TCNP})$, determined from the slope of the plot of ln $I_P(t)$ *versus* t in the range between $t_1 = 1000$ s and $t_2 = 1500$ s, is found to be $k_{H^+}(\text{TCNP}) = 2.2 \times 10^{-3}$ s^{-1} at $T = 15$ °C. This value agrees very well, within the error limits of about 15%, with the value of the pseudo first-order rate constant $k_s'(\text{NPCF})$ obtained for the

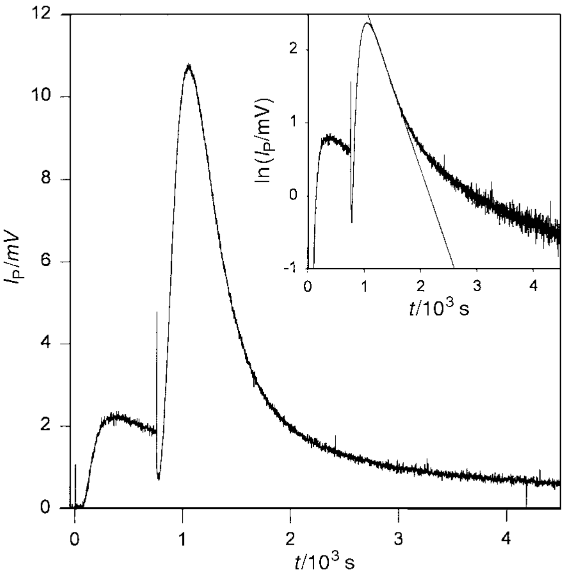


Fig. 4 $I_P(t)$ as a function of time for the system TCNP–H_2O_2 in THF in the presence of H_2SO_4 (added after 750 s). The inset presents the corresponding plot of ln $I_P(t)$ *versus* time. Conditions: [TCNP] = [H_2O_2] = 5.2×10^{-2} mol dm^{-3}; [H^+] = 2.00×10^{-2} mol dm^{-3} at t = 750 s; T = 15 °C.

NPCF–H_2O_2 system with [NPCF] = 2.00×10^{-2} mol dm^{-3} and [H_2O_2] = 3.96×10^{-1} mol dm^{-3} (see the corresponding square in Fig. 3).

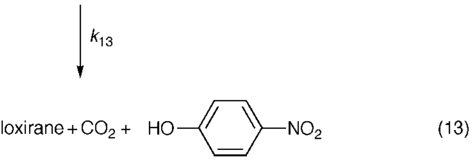
Furthermore we have performed measurements at T = 15 °C using the same conditions for the TCNP–H_2O_2 system as described above with sulfuric acid concentrations of 1.0×10^{-2} mol dm^{-3} and 5.0×10^{-2} mol dm^{-3}. Similar $I_P(t)$ curves, after addition of sulfuric acid, were observed to those presented in Fig. 4. The values of k_{H^+}(TCNP) obtained are: k_{H^+}(TCNP) = 1.1×10^{-3} s^{-1} at [H^+] = 1.0×10^{-2} mol dm^{-3} and k_{H^+}(TCNP) = 3.8×10^{-3} s^{-1} at [H^+] = 5.0×10^{-2} mol dm^{-3}. Again these values agree very well, within the error limits, with the corresponding values of the plot log k_s'(NPCF) *versus* log [NPCF] (see the corresponding squares in Fig. 3).

From the agreement of the values of k_{H^+}(TCNP) with the values of k_s'(NPCF) it can be deduced that in both the TCNP–H_2O_2–H_2SO_4 system and the NCPF–H_2O_2 system the *in situ* generated *O*-*p*-nitrophenyl monoperoxcarbonic acid **1** decomposes *via* the same mechanism presented in Scheme 2.

G. Investigations concerning the reactivity of the NPCF–H_2O_2 system towards olefins

According to the mechanism presented in Scheme 2 carbon trioxide is formed in the NPCF–H_2O_2 system. Carbon trioxide should be a powerful epoxidizing agent. This assumption is confirmed by the results of our measurements carried out with both the NPCF–H_2O_2 and the TCNP–H_2O_2 system in THF using (*E*)-stilbene.

The results obtained for the TCNP–H_2O_2 system are depicted in Fig. 5. It is seen that $^1O_2$ can be detected under the conditions used and, as expected, the higher the concentration of (*E*)-stilbene the lower the amount of $^1O_2$ liberated. The fact that $^1O_2$ is observed indicates that reaction (6) between **1** and hydrogen peroxide (to produce, most likely, the diperoxycarbonic acid **2** as precursor of $^1O_2$) clearly competes with the epoxidation of *E*-stilbene described by eqn. (13).



(13)

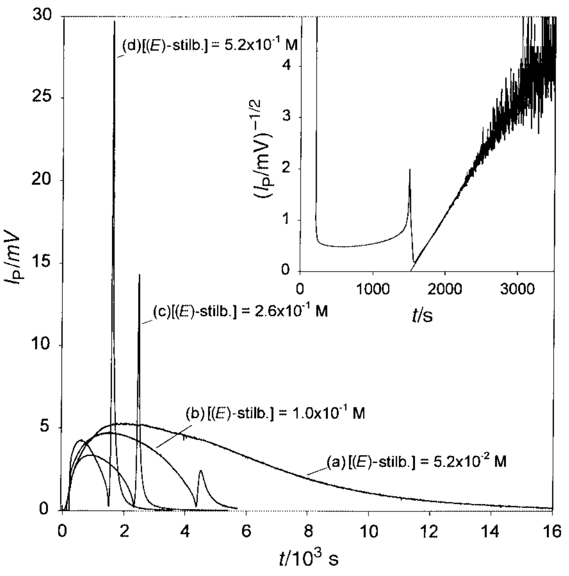


Fig. 5 $I_P(t)$ as a function of time for the system TCNP–H_2O_2–(*E*)-stilbene (*E*-stilb.) in THF at different (*E*)-stilbene concentrations. The inset shows the plot of $1/\sqrt{I_P(t)}$ *versus* time for curve d. Conditions: [TCNP] = 5.20×10^{-2} mol dm^{-3} [H_2O_2] = 5.20×10^{-1} mol dm^{-3}; $5.2 \times 10^{-2} \leq$ [*E*-stilb.] $\leq 5.2 \times 10^{-1}$ mol dm^{-3}; T = 20 °C. M denotes the concentration in mol dm^{-3}.

The $I_P(t)$ curves b, c and d exhibit at the end a narrow $I_P(t)$ signal. The intensity of the narrow signal increases as the olefin concentration increases. These signals conform to a second-order reaction for which the plot of $1/\sqrt{I_P(t)}$ *versus* time should give a straight line.[1,19] This is observed, *e.g.*, for the corresponding plot of the narrow signal of curve d (see the inset in Fig. 5).

The narrow signals observed are no artefacts. Similar signals were also observed in the TCNP–H_2O_2 system in the presence of cyclohexene.[1] In this case we could show that the signals were caused, most probably, by a bimolecular reaction between **1** and the 1,2-epoxycyclohexane originally generated in the system. To test whether **1** is also able to react with *trans*-1,2-diphenyloxirane to give $^1O_2$ we have performed measurements with the TCNP–H_2O_2 system in THF in the presence of *trans*-1,2-diphenyloxirane. But no $^1O_2$ could be detected. Thus no plausible explanation can as yet be offered for the narrow signals. However, it is evident that the amount of $^1O_2$ generated in the unknown second-order reaction is small.

The data found for the TCNP–olefin–H_2O_2 system[1] are consistent with the assumption that in this system only one peroxy intermediate is the epoxidizing agent, namely the *O*-*p*-nitrophenyl monoperoxycarbonic acid **1**. If this holds also true for the NPCF–olefin–H_2O_2 system, it must be expected that $^1O_2$ can be detected, *e.g.*, in the presence of a 10-fold excess of (*E*)-stilbene. This is especially the case if reaction (7) is distinctly faster than reaction (6) under comparable conditions (*vide supra*) and consequently in the NPCF–(*E*)-stilbene–H_2O_2 system **1** should be mainly consumed by reaction (7) producing CO_3 as the precursor of $^1O_2$.

However, when hydrogen peroxide is added in 10-fold excess to a THF solution of NPCF (2.0×10^{-2} mol dm^{-3}) containing a 10-fold excess of (*E*)-stilbene no $^1O_2$ is observed for about one hour. Moreover, to demonstrate that in the presence of (*E*)-stilbene the $^1O_2$ generation in the TCNP–H_2O_2 system is suppressed, we have added the instantly soluble crystalline (*E*)-stilbene to a THF solution of NCPF and H_2O_2 after t > 200 s. The result of such experiment is depicted in Fig. 6. Under the conditions used an induction period of about 90 s is observed, after which $I_P(t)$ increases up to about 11 mV. After 300 s (*E*)-stilbene was added, resulting in the drastic suppres-

$$H_2O_2 + Cl^- + H^+ \xrightarrow[\text{(slow)}]{k_{14}} HOCl + H_2O \qquad \Delta G_R^0 = -51.62\ \text{kJ mol}^{-1} \qquad (14)$$

$$HOCl + H^+ + Cl^- \underset{\substack{k_{-15}\\ \text{(fast)}}}{\overset{k_{15}}{\rightleftharpoons}} Cl_2 + H_2O \qquad \Delta G_R^0 = -19.02\ \text{kJ mol}^{-1} \qquad (15)$$

$$HOCl + H_2O_2 \xrightarrow[\substack{\text{(slow)}\\ \text{but faster than (14)}}]{k_{16}} {}^1O_2 + H^+ + Cl^- + H_2O \qquad \Delta G_R^0 = -60.04\ \text{kJ mol}^{-1} \qquad (16)$$

the sum of (14) and (15) is reaction (17)

$$H_2O_2 + 2H^+ + 2\,Cl^- \longrightarrow Cl_2 + 2H_2O \qquad \Delta G_R^0 = -70.94\ \text{kJ mol}^{-1} \qquad (17)$$

the sum of (15) reversed and (16) is reaction (18)

$$H_2O_2 + 2Cl_2 \longrightarrow {}^1O_2 + 2H^+ + 2\,Cl^- \qquad \Delta G_R^0 = -41.01\ \text{kJ mol}^{-1} \qquad (18)$$

Scheme 3

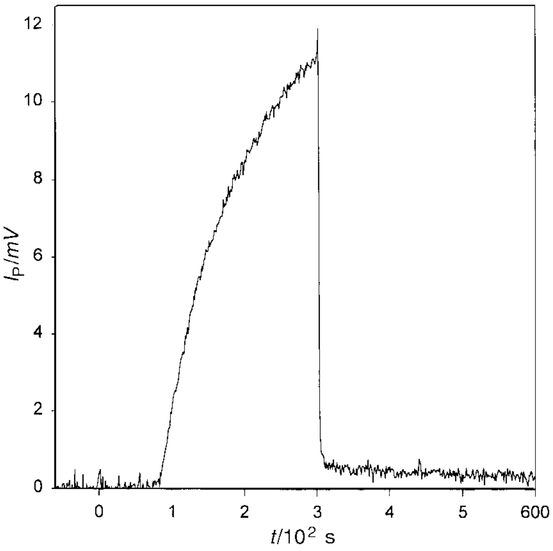


Fig. 6 $I_P(t)$ as a function of time for the system NPCF–H_2O_2 in THF with crystalline (*E*)-stilbene added after 300 s. Conditions: [NPCF] = 2.0×10^{-2} mol dm^{-3}; [H_2O_2] = 2.0×10^{-1} mol dm^{-3}; [(*E*)-stilbene] = 1.0×10^{-1} mol dm^{-3} related to the reaction volume; $T = 15$ °C.

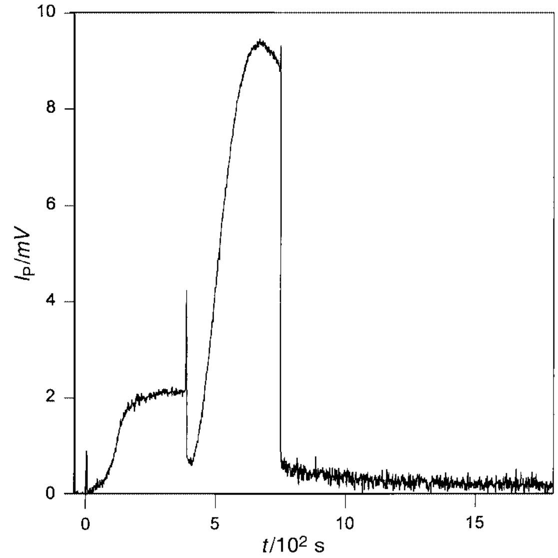


Fig. 7 $I_P(t)$ as a function of time for the system TCNP–H_2O_2 in THF with sulfuric acid added after 380 s and (*E*)-stilbene added after 750 s. Conditions: [TCNP] = [H_2O_2] = 5.2×10^{-2} mol dm^{-3}; [H^+] = 2.0×10^{-2} mol dm^{-3}; [(*E*)-stilbene] = 2.6×10^{-1} mol dm^{-3} related to the reaction volume; $T = 15$ °C.

sion of $^1O_2$ generation. However, the formation of $^1O_2$ is not completely suppressed.

The same behaviour is observed for the TCNP–H_2O_2–sulfuric acid system as demonstrated in Fig. 7. To a TCNP–H_2O_2 system with [TCNP] = [H_2O_2] = 5.0×10^{-2} mol dm^{-3} in THF, sulfuric acid ([H^+] = 2×10^{-2} mol dm^{-3}) was added after about 380 s. In agreement with the observation made in the experiment described in Fig. 4, $I_P(t)$ decreases shortly after the addition of sulfuric acid, but then $I_P(t)$ increases considerably. After the maximum is reached, solid (*E*)-stilbene ([(*E*)-stilbene] = 2.6×10^{-1} mol dm^{-3} related to the reaction volume) was added to the solution at about 750 s. This results in a comparable suppression of $^1O_2$ formation as observed for the NPCF–H_2O_2–(*E*)-stilbene system.

Similar attempts using cyclohexene have shown that after addition of this olefin to a NPCF–H_2O_2 system or a TCNP–H_2O_2-sulfuric acid system, in both systems the formation of $^1O_2$ is totally suppressed.

Summarizing the results it can be deduced: i) that in the NPCF–H_2O_2 system as well as in the TCNP–H_2O_2 system **1** is primarily generated; ii) that in the NPCF–H_2O_2 system and in the TCNP–H_2O_2–sulfuric acid system, respectively, an acid-catalysed decomposition of **1** occurs according to an $A_{AC}1$-mechanism to produce carbon trioxide and; iii) that carbon trioxide is a more powerful oxidizing agent than **1**.

H. Chloride-catalysed decomposition of hydrogen peroxide

That the chloride-catalysed decomposition of hydrogen peroxide in acidic solution might be expected to generate $^1O_2$ follows from a consideration of the free enthalpies of the substances involved. The mechanism of the catalysis postulated by Livingston and Bray[11] is outlined in Scheme 3. In this mechanism the reaction between hydrogen peroxide and chloride to give water and the hypochlorite ion (ClO^-) (ref. 12) and the formation of chlorine hydroperoxide (HOOCl) postulated by Connick[13] are not taken into account. The values of the free enthalpies ΔG^f_{298} of the different substances[20] used for the

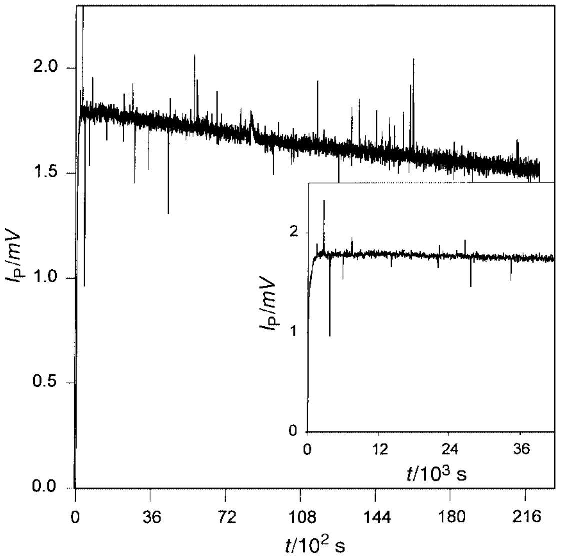


Fig. 8 $I_P(t)$ as a function of time for the HCl–H_2O_2 system in water. The inset represents the $I_P(t)$ curve observed for the first hour. Conditions: [HCl] = 2.0 mol dm^{-3}; [H_2O_2] = 5.0 mol dm^{-3}; [Dequest] = 1.0×10^{-3} mol dm^{-3}; $T = 20$ °C.

calculation of the reaction enthalpy $\Delta G_R{}^0$ are given below as footnote.‡

It is seen that the $\Delta G_R{}^0$ terms for the reactions considered have negative values, thus the chloride-catalysed decomposition of hydrogen peroxide in acidic solution should generate $^1O_2$. This is in agreement with the results obtained for the NPCF–H_2O_2 system (see Fig. 1 at $t > 1500$ s), for the HCl–H_2O_2 system in THF and for the HCl–H_2O_2 system in water (see Fig. 8).

For a HCl–H_2O_2 system ([HCl] = 2.0×10^{-1} mol dm^{-3}; [H_2O_2] = 1.0×10^{-1} mol dm^{-3}) in THF at $T = 10$ °C it was observed that after addition of hydrogen peroxide to the hydrochloric acid–THF solution the $^1O_2$ phosphorescence intensity I_P increases gradually for 2000 s up to $I_P = 3.0$ mV and that at this time the steady state is reached. At $t > 2000$ s the rate of $^1O_2$ formation was found to be constant over a long time interval.

In contrast, the steady state is reached in the HCl–H_2O_2 systems in water within about 3 minutes from the addition of hydrogen peroxide to the hydrochloric acid solution. This is demonstrated in Fig. 8. However, again, if the steady state is reached the rate of $^1O_2$ formation does not change appreciably. As the inset of Fig. 8 shows, over one hour the rate of $^1O_2$ formation is actually constant. That means that the concentration of hydrogen peroxide also does not change markedly over a longer time interval. The same observation has already been made by Mohammad and Liebhafsky in acidic solution[12] and by Evans and Upton in neutral solution.[21] In the following, the aqueous HCl–H_2O_2 system should be regarded in more detail, since for this system the mechanism given in Scheme 3 is established. According to this mechanism eqn. (19) holds if the

$$\frac{d[\mathrm{HOCl}]_f}{dt} = k_{14}[\mathrm{H^+}]_s[\mathrm{Cl^-}]_s[\mathrm{H_2O_2}]_s = \frac{d[\mathrm{HOCl}]_d}{dt} \qquad (19a)$$

$$\frac{d[\mathrm{HOCl}]_d}{dt} = \frac{d[^1\mathrm{O_2}]}{dt} = k_{16}[\mathrm{HOCl}]_s[\mathrm{H_2O_2}]_s \qquad (19b)$$

steady state is reached. In this case the rate of hypochlorous acid formation d[HOCl]$_f$/dt is equal to the rate of hypochlorous acid disappearance d[HOCl]$_d$/dt and consequently equal to the rate of $^1O_2$ formation d[$^1O_2$]/dt. The subscript s refers to the concentrations at the steady state.

Table 1 Kinetic data of the chloride-catalysed decomposition of hydrogen peroxide in aqueous acidic solution. Conditions: [HCl] = 2.0 mol dm^{-3}; [H_2O_2] = 5.0 mol dm^{-3}

T/K	(d[$^1O_2$]/dt)/ mol dm^{-3} s^{-1}	k_{14}/dm^6 mol^{-2} s^{-1}
283	7.2×10^{-6}	3.6×10^{-7}
293	2.2×10^{-5}	1.1×10^{-6}
303	7.8×10^{-5}	3.9×10^{-6}

From the "constant" $I_P(t)$ values the rate of $^1O_2$ formation can be evaluated according to eqn. (1), (see Table 1). But, the knowledge of the d[$^1O_2$]/dt value does not enable us to evaluate k_{16}, since, especially for the steady concentration of hypochlorous acid, no plausible value is known. For the calculation of k_{14} the initial concentrations of hydrochloric acid and hydrogen peroxide are used assuming that these values do not differ markedly from the corresponding steady state values.

The value of $k_{14} = (1.1 \pm 0.3) \times 10^{-6}$ dm^6 mol^{-2} s^{-1} at $T = 20$ °C calculated from the $I_P(t)$ value presented in Fig. 8 is of the same order of magnitude as the values reported for the aqueous HCl–H_2O_2 system at $T = 25$ °C (8.3×10^{-7} dm^6 mol^{-2} s^{-1}).[12,14a] This fact has encouraged us to perform measurements at different temperatures. At $T = 10$ and $T = 30$ °C the aqueous HCl–H_2O_2 system shows the same behaviour as at $T = 20$ °C, *i.e.* over a longer time interval a constant rate of $^1O_2$ formation is observed, thus the values of d[$^1O_2$]/dt and k_{14} can be calculated. These values are given in Table 1. From the corresponding Arrhenius plot the apparent Arrhenius parameters $E_{aa} = (85 \pm 8)$ kJ mol^{-1} and ln $A_a = (22 \pm 1)$ are obtained. These values are in excellent agreement with the values reported by Mohammad and Liebhafsky,[12] taking into account that the values of A_a reported have the unit dm^6 mol^{-2} min^{-1}. Consequently the values obtained for k_{14} (this paper) agree within the error limits with the values of k_1 given in ref. 12. This indicates that the method used for the calculation of k_{14} yields reasonable values.

At $T = 20$ °C we have measured $I_P(t)$ over about 6 hours. In this case the decrease of $^1O_2$ formation is distinctly observed. For the change of $I_P(t)$ eqn. (20) holds, indicating that $I_P(t)$

$$I_P(t) = Ck_{obs}[\mathrm{H_2O_2}]_0 e^{-k_{obs}t} \qquad (20)$$

should decrease according to a pseudo first-order reaction. [H_2O_2]$_0$ denotes the initial concentration of hydrogen peroxide and k_{obs} is described by eqn. (21).

$$k_{obs} = 2k_{14}[\mathrm{H^+}][\mathrm{Cl^-}] \qquad (21)$$

According to eqn. (20) the plot of ln $I_P(t)$ *versus* time yields a straight line with the slope equal to $-k_{obs}$. k_{obs} was determined to be $k_{obs} = 7.7 \times 10^{-6}$ s^{-1} and with [H^+] = [Cl^-] = 2.0 mol dm^{-3} for k_{14} a value of $k_{14} = 9.6 \times 10^{-7}$ dm^6 mol^{-2} s^{-1} is obtained, which agrees excellently with the value of k_{14} calculated from the "constant" $I_P(t)$ value observed for the first hour (see Fig. 8).

Although, for the chloride-catalysed decomposition of hydrogen peroxide a 100% yield of $^1O_2$ would be expected according to the $\Delta G_R{}^0$ values given in Scheme 3, only a 8.4% yield of $^1O_2$ was detected by measuring the chloride–H_2O_2 system in neutral solution at $T = 50$ °C using a chemical trap for $^1O_2$ detection.[21] As yet no measurements were performed with the IR-chemiluminescence method to determine the yield of $^1O_2$ in acidic solutions.

On the basis of the $I_P(t)$ curve depicted in Fig 8 we can prove whether the oxygen is exclusively formed as $^1O_2$, although the change in concentration of hydrogen peroxide is relatively small within the time scale of about 6 hours. Fig. 9 shows the plot of the concentration of $^1O_2$ *versus* the values of

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‡ $\Delta G^f_{298}(H_2O)_l = -237.18$ kJ mol^{-1}; $\Delta G^f_{298}(H_2O_2) = -134.10$ kJ mol^{-1}. $\Delta G^f_{298}(^1O_2) = 94.20$ kJ mol^{-1} (0.976 eV); $\Delta G^f_{298}(Cl_2)_{aq} = 7.20$ kJ mol^{-1}. $\Delta G^f_{298}(Cl^-) = -131.06$ kJ mol^{-1}; $\Delta G^f_{298}(HOCl)_{aq} = -79.90$ kJ mol^{-1}.

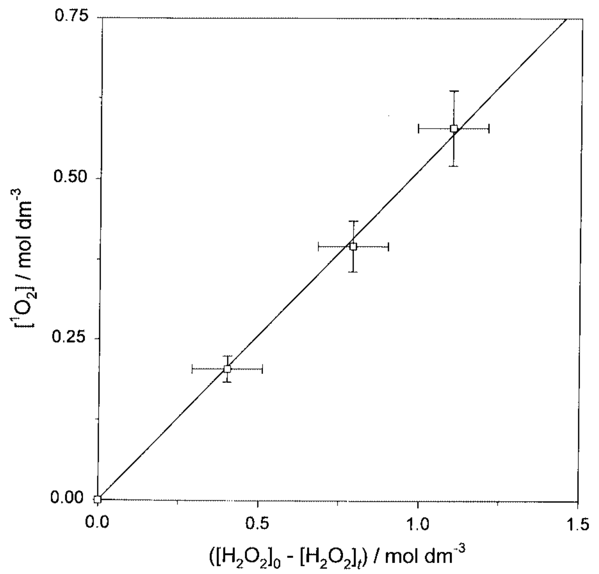

Fig. 9 Plot of $[^1O_2]$ *versus* $[H_2O_2]_0 - [H_2O_2]_t$, determined at 2, 4 and 6 hours, of the aqueous HCl–H_2O_2 system. Conditions: see Fig. 8.

$[H_2O_2]_0 - [H_2O_2]_t$ determined by cerimetric titration at three different times. The concentration of $^1O_2$ was evaluated according to eqn. (2).

According to the mechanism presented in Scheme 3 the rate of $^1O_2$ formation should be half the rate of hydrogen peroxide disappearence and consequently the plot of $[^1O_2]$ *versus* $[H_2O_2]_0 - [H_2O_2]_t$ should yield a straight line with a slope of $S = 0.50$, which is experimentally observed within the error limits.

Concluding remarks

The postulated formation of carbon trioxide induced by an acid catalysed ester-bond cleavage of the *O*-*p*-nitrophenyl monoperoxycarbonic acid may not be a singular case.

In principle *O*-alkyl and other *O*-aryl monoperoxycarbonic acids might be considered as precursors for the formation of carbon trioxide. Furthermore *N*-acyl and *N*-arylsulfonylperoxycarbamic acids can also be regarded as potential precursors for the formation of carbon trioxide.

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