PERKIN 2

Nucleophilic activation of hydrogen peroxide. On the formation and the reactivity of 1*H*-1,2,4-triazoleperoxycarboxylic acid and *O*-*p*-nitrophenylmonoperoxycarbonic acid †

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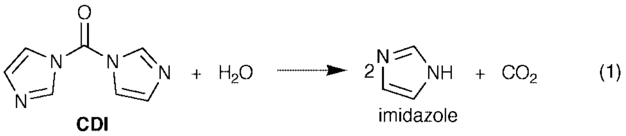
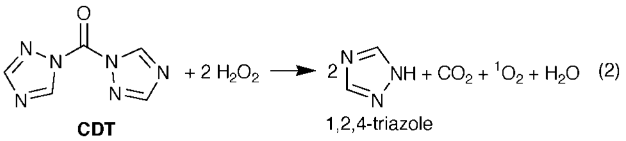
Measurements of the infrared phosphorescence of singlet molecular oxygen ($^1O_2$) at 1270 nm have been employed to demonstrate the formation of $^1O_2$ in the system *N*,*N′*-carbonyldi-1,2,4-triazole (CDT)–hydrogen peroxide and in the system 1*H*-1,2,4-triazolecarboxylic acid *p*-nitrophenyl ester (TCNP)–hydrogen peroxide in tetrahydrofuran. At hydrogen peroxide concentrations of $[H_2O_2] \geq 2$ [CDT] or ≥ 2 [TCNP] one molecule of $^1O_2$ is generated per molecule of CDT and TCNP, respectively. In both systems a very reactive peroxy-intermediate is formed. In the system CDT–H_2O_2 the 1*H*-1,2,4-triazoleperoxycarboxylic acid (**1**) is generated, in TCNP–H_2O_2 the *p*-nitrophenylmonoperoxycarbonic acid (**4**). For the epoxidation of cyclohexene in THF by **1** a rate constant $k_{15} \approx 3 \times 10^0$ dm^3 mol^{-1} s^{-1} can be estimated. For **4** the corresponding rate constant was found to be $k_{20} \approx 6 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}. The Arrhenius parameters of the formation of **1** and **4**, respectively, and in addition of their consecutive reactions with hydrogen peroxide were determined. The results are consistent with the assumption that the nucleophilic displacements by hydrogen peroxide at the carbonyl carbon atom are addition–elimination processes, which take the form of a $B_{AC}2$-mechanism.

Introduction

Staab[1] was the first to demonstrate that the carbonyl group of diazolides of carbonic acid is strongly electronically activated on account of the two electron-withdrawing heterocycles. *N*,*N′*-carbonyldiimidazole (CDI), *e.g.*, reacts with pure water at room temperature within a few seconds to give two molecules of imidazole and one molecule of carbon dioxide.

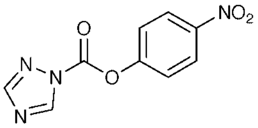


Since hydrogen peroxide is more nucleophilic than water[1] it is not surprising that azolides (*N*-acetylazoles) of the carbonic acid also react with hydrogen peroxide. Rebek *et al.*[2] have investigated the system *N*,*N′*-carbonyldi-1,2,4-triazole (CDT)–H_2O_2 in different organic solvents and postulated that 1*H*-1,2,4-triazoleperoxycarboxylic acid as a reactive peroxy-intermediate is produced which effectively epoxidizes olefins like cyclohexene (*vide infra*). Moreover, the authors have observed that in this system, in the absence of olefins, molecular singlet oxygen ($^1O_2$) is quantitatively formed according to eqn. (2).



In contrast to the system CDT–H_2O_2, the system CDI–H_2O_2 was found to be ineffective with respect to the epoxidation of olefins and no $^1O_2$ generation was observed.[2]

Up to now the mechanism of $^1O_2$ formation in the system CDT–H_2O_2 postulated by Rebek *et al.*[2] was not studied in detail. To get more insight into the kinetics of reaction (2) we have investigated this reaction in tetrahydrofuran (THF) by measuring the formation of $^1O_2$ on the basis of the $^1O_2$ phosphorescence at $\lambda = 1270$ nm.[3] Additionally, employing the same method we have studied the system CDI–H_2O_2 and the system 1*H*-1,2,4-triazolecarboxylic acid *p*-nitrophenyl ester (TCNP)–H_2O_2.


TCNP

Experimental

Materials

The following compounds and solvents, respectively, were purchased from Fluka and used as received: *N*,*N′*-carbonyldiimidazole (CDI) (*purum*, ~97%, mp 112–115 °C), *N*,*N′*-carbonyldi-1,2,4-triazole (CDT) (≥98%, mp 145–150 °C), *N*-(trimethylsilyl)-1,2,4-triazole (*puriss.* ≥99% (GC)), 4-nitrophenyl chloroformate (*purum*, ≥97%), cyclohexene (*puriss.* p.a.), 9,10-dimethylanthracene (DMA) (*purum*, ~97%), THF (for HPLC), chloroform ($CHCl_3$ for IR-spectroscopy) and diethyl ether (Et_2O, *puriss.* ≥99.5%; $H_2O \leq 0.005\%$). Benzene (*p.a.*, $H_2O < 0.03\%$) was obtained from Riedel-de Haën. 30% Hydrogen peroxide (pract.) came from Merck. CDI, CDT and the stabilizer free THF from Fluka were stored under dry nitrogen. Water free solutions of hydrogen peroxide in $CHCl_3$ and Et_2O were prepared according to literature procedure.[4]

Preparation of 1*H*-1,2,4-triazolecarboxylic acid *p*-nitrophenyl ester (TCNP)

p-Nitrophenyl chloroformate (6.9 g, 34 mmol) was dissolved in 30 mL of dry benzene. A solution of 5 mL of *N*-(trimethylsilyl)-

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† The IUPAC name for carbonic acid is hydroxyformic acid.

1,2,4-triazole (34 mmol) in 30 mL of dry benzene was added dropwise to the stirred solution of the chloroformate at room temperature. After addition was completed the mixture was stirred for another 15 minutes, while precipitation of the product was observed. The product was filtered and washed with dry benzene and dried *in vacuo*. The yield of the product was 5.9 g (72%), mp 144–146 °C (Found: C, 46.06; H, 2.69; N, 23.96. $C_9H_6N_4O_4$ requires: C, 46.13; H, 2.58; N, 23.93%); ν_{max}/cm^{-1} 3400 (>C=N-), 1600, 1580 and 1500 (C=C), 1790 (C=O), 1530 and 1320 (N=O), 1290 (C–O). Infrared spectra were taken on a Philips model IR-PU 9700 infrared spectrometer and were run as potassium bromide pellets.

Gas volumetric measurements

The gas volumetric measurements were carried out according to the procedures described by Rebek *et al.*[2] For determination of the purity of CDT the amount of CO_2 evolved in the reaction between CDT and double distilled water at $T = 25$ °C was measured. 95 mg of CDT yielded 12.7 mL of CO_2 (90% of theoretical yield).

Moreover, we have measured the volumes of gases evolved in the reactions between CDT and 30% hydrogen peroxide both in the absence and in the presence of cyclohexene and 9,10-dimethylanthracene, respectively.

Singlet oxygen infrared emission measurements

The near-infrared luminescence (IRL) spectrometer used in our studies for recording the steady state $^1O_2$ phosphorescence emission at $\lambda = 1270$ nm has been described in detail.[3,5–7]

For the intensity of the $^1O_2$ phosphorescence emission, I_P, eqn. (3) holds,[6] where c is a constant of the IRL spectrometer,

$$I_P(t) = ck_P\tau_\Delta \frac{d[^1O_2]}{dt} \qquad (3)$$

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.

If the product $C = c\ k_p\ \tau_\Delta$ is known for a given solvent or a solvent mixture, the concentration of $^1O_2$ can be calculated from the plot of $I_P(t)$ *versus* time according to eqn. (4). The

$$[^1O_2] = \frac{1}{C}\int_{t=0}^{t=\infty} I_P(t)dt \qquad (4)$$

value of c strongly depends on the sensitivity of the germanium diode. In our measurements two different germanium diodes of the type North Coast EO 817L were employed. For the older one a value of $c_1 = (3.0 \pm 0.2) \times 10^{11}$ mV dm^3 s mol^{-1} (ref. 6) was determined and for the new one a value of $c_2 = (1.4 \pm 0.1) \times 10^{11}$ mV dm^3 s mol^{-1} was obtained.

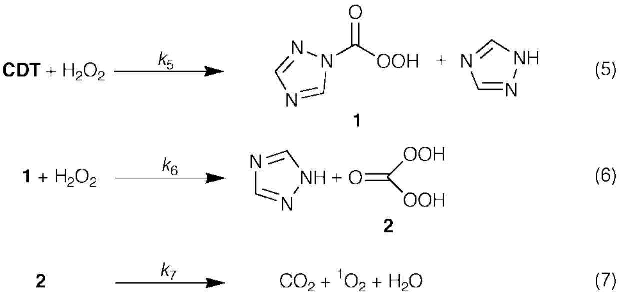
The values of τ_Δ of the solvent mixtures (THF–H_2O_2 (30%)) were directly measured with our home built IRL spectrometer.[3] The values obtained are presented below. For the calculation of the amount of $^1O_2$ evolved in the different systems a value of $k_p = (0.45 \pm 0.10)$ s^{-1} was used, which agrees very well within the error limits with k_p values determined for pure THF.[8]

Reactions were carried out in thermostatted 1 cm quartz cuvettes. To the THF solutions of CDT, CDI and TCNP 30% hydrogen peroxide was added by a micro syringe. Vigorous stirring was necessary. The initial concentrations of CDT and TCNP used are given in the legends of the figures or in the text.

Table 1 Results of the volumetric measurements of the reaction of *N*,*N*′-carbonyldi-1,2,4-triazole (CDT) with 30% hydrogen peroxide in THF at $T = 25$ °C; [CDT] = 1.0×10^{-1} mol dm^{-3}

System	$\overline{\text{equiv.}}$[a]	$\overline{\text{equiv.}}_{corr} = \frac{\overline{\text{equiv.}}(H_2O_2)}{\overline{\text{equiv.}}(H_2O)}$
CDT–H_2O[b]	0.9 ± 0.1	—
CDT–H_2O_2[c]	1.8 ± 0.1	2.0
CDT–H_2O_2–DMA[d]	0.9 ± 0.2	1.0
CDT–H_2O_2–cyclohexene[e]	1.0 ± 0.1	1.1

[a] Mean value of 3 measurements. [b] $[H_2O] = 100 \times$ [CDT]. [c] $[H_2O_2] = 20 \times$ [CDT]. [d] Solution saturated with DMA, $[H_2O_2] = 15 \times$ [CDT]. [e] $[H_2O_2]$ = [cyclohexene] = $15 \times$ [CDT].



Scheme 1

Rate law and expression for $I_P(t)$

For reaction (2) Rebek *et al.*[2] have postulated a three step mechanism, shown in Scheme 1. In the first step 1*H*-1,2,4-triazoleperoxycarboxylic acid (**1**) should be generated which, moreover, should react with hydrogen peroxide in the second step to give most probably the elusive diperoxycarbonic acid (**2**). Assuming that **2** is unstable (with respect to the properties of **2** no prediction was made[2]) and generates in the third step very fast finally CO_2, H_2O and $^1O_2$, then the rate of $^1O_2$ formation is determined by the competitive, consecutive second-order reactions (5) and (6).[9]

The particular difficulty of such a type of reaction is that the reaction steps are second-order. However, the solution is simpler when hydrogen peroxide is in large excess and thus we have in effect two successive first-order reactions.

Under first-order conditions for $I_P(t)$ eqn. (8) can be derived,

$$I_P(t) = Ck_6'[\text{CDT}]_0 \frac{k_5'}{k_6' - k_5'}\{\exp(-k_5't) - \exp(-k_6't)\} \qquad (8)$$

where C represents the product $c\ k_p\ \tau_\Delta$, $[\text{CDT}]_0$ is the initial concentration of CDT and $k_5' = k_5[H_2O_2]$ and $k_6' = k_6\ [H_2O_2]$ denote the pseudo first-order rate constants of reactions (5) and (6), respectively. The rate constant of the slow reaction can be evaluated from the plot of ln $I_P(t)$ *versus t* which yields at longer reaction time a straight line with the slope equal to k_5' or k_6' (*vide infra*). 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 in eqn. (9).

$$t_{max} = \frac{1}{k_6' - k_5'}\ln\left(\frac{k_6'}{k_5'}\right) \qquad (9)$$

It must be noted that on the basis of eqn. (8) or eqn. (9) it cannot be deduced which of the reactions is the faster one.

Results and discussion

A. Investigation of the system *N*,*N*′-carbonyldi-1,2,4-triazole (CDT)–H_2O_2

A.1 Gas volumetric measurements. First we performed gas volumetric measurements with the system CDT–H_2O_2 using 30% hydrogen peroxide. The results summarized in Table 1 agree excellently with the data of Rebek *et al.*,[2] who used 98% hydrogen peroxide for their measurements. In the absence of olefins or $^1O_2$ acceptors 2.0 equiv. of gas are generated. When

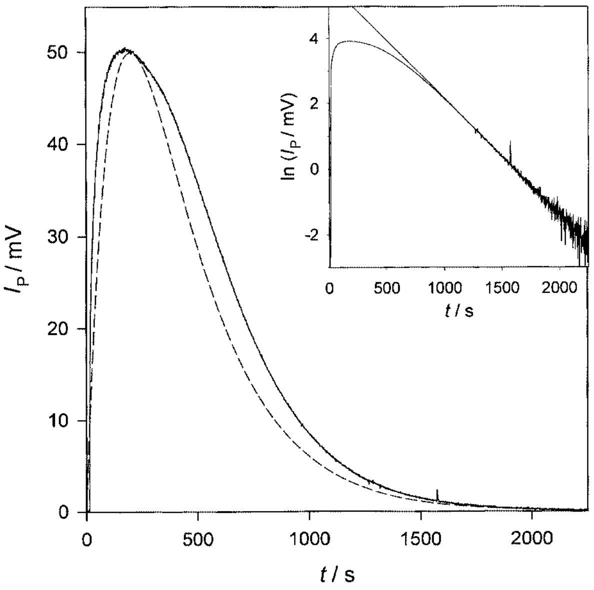


Fig. 1 $I_P(t)$ as a function of time of the system CDT–H_2O_2 in THF. The inset shows the corresponding plot of ln $I_P(t)$ *versus* time. Conditions: [CDT] = 1.25×10^{-2} mol dm^{-3}; [H_2O_2] = 1.25×10^{-1} mol dm^{-3}; $T = 10$ °C. —— = experimental curve; ---- = theoretically calculated curve according to eqn. (8) using $c_1 = (3.0 \pm 0.2) \times 10^{11}$ mV dm^3 s mol^{-1}; $k_p = (0.45 \pm 0.10)$ s^{-1} and $\tau_\Delta = (18 \pm 1)$ µs; k_f'(CDT) = 7.2×10^{-3} s^{-1}; k_s'(CDT) = 3.4×10^{-3} s^{-1}.

the THF solution contains excess cyclohexene, or is saturated with DMA only 1.0 equiv. of gas is evolved. The observation that the results of the gas volumetric measurements are independent of the percentage of hydrogen peroxide (98% or 30%) is consistent with the fact that hydrogen peroxide is more nucleophilic than water.[1]

A.2 $^1O_2$ phosphorescence intensity as a function of time. Fig. 1 shows a plot of $I_P(t)$ *versus* time of the system CDT–H_2O_2. The shape of this curve is consistent with eqn. (8). In accordance with a consecutive reaction for the $^1O_2$ formation an induction period (here about 20 s) is observed. The plot of ln $I_P(t)$ *versus* time, depicted in the inset of Fig. 1, results in a straight line at about $t \geq 800$ s with a slope equal to $-k_s'$(CDT), the rate constant of the slow reaction (*vide supra*).

With the values of k_s'(CDT) and $t_{max} = 253$ s the rate constant k_f'(CDT) of the faster reaction can be estimated according to eqn. (9). At $T = 10$ °C the pseudo first-order rate constants were found to be k_f'(CDT) = $(7.2 \pm 1.2) \times 10^{-3}$ s^{-1}; k_s'(CDT) = $(3.4 \pm 0.4) \times 10^{-3}$ s^{-1}. With [H_2O_2] = 1.25×10^{-1} mol dm^{-3} for the corresponding second-order rate constants the following values can be calculated: $k_f = (5.8 \pm 1.0) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}; $k_s = (2.7 \pm 0.3) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}.

As already mentioned, *a priori* it cannot be decided which of the two rate constants is connected with reaction (5) or reaction (6). This question will be discussed after the presentation of further experimental results.

According to eqn. (4) the concentration of $^1O_2$ generated in the system CDT–H_2O_2 can be evaluated from the area under the $I_P(t)$→t curve between $t = 20$ s and $t = 2250$ s. The area was found to be $ar = (34100 \pm 4\%)$ mV s. With the values of c_1, k_p and τ_Δ given in the legend of Fig. 1 for the concentration of $^1O_2$ a value of [$^1O_2$] = $(1.4 \pm 0.3) \times 10^{-2}$ mol dm^{-3} can be estimated, whereby the error limit is mainly determined by the uncertainty of k_p. The value of [$^1O_2$] obtained agrees very well within the error limits with the initial concentration of [CDT] = 1.25×10^{-2} mol dm^{-3} and confirms the result of the gas volumetric measurements which have also shown that according to eqn. (2) one molecule of CDT yields at least one $^1O_2$ molecule.

Fig. 1 also shows the $I_P(t)$→t curve theoretically estimated according to eqn. (8). The values of the different parameters used for the estimation are given in the legend of Fig. 1. As one can see the experimental and theoretical curves do not completely cover one another, but the difference between the areas lies within the error limits of about 15%.

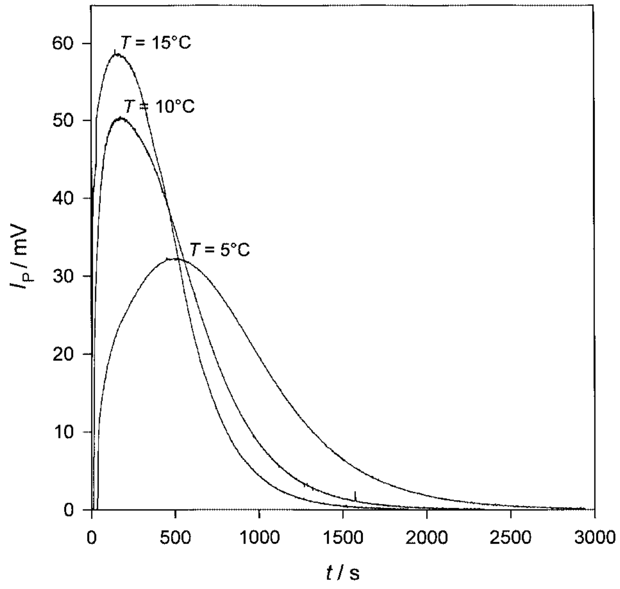


Fig. 2 Plots of $I_P(t)$ *versus* t of the system CDT–H_2O_2 in THF determined at three different temperatures. Conditions: [CDT] = 1.25×10^{-2} mol dm^{-3}; [H_2O_2] = 1.25×10^{-1} mol dm^{-3}.

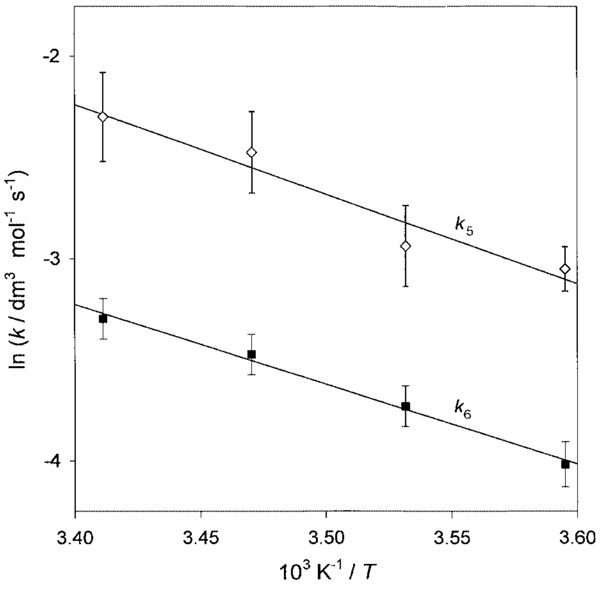


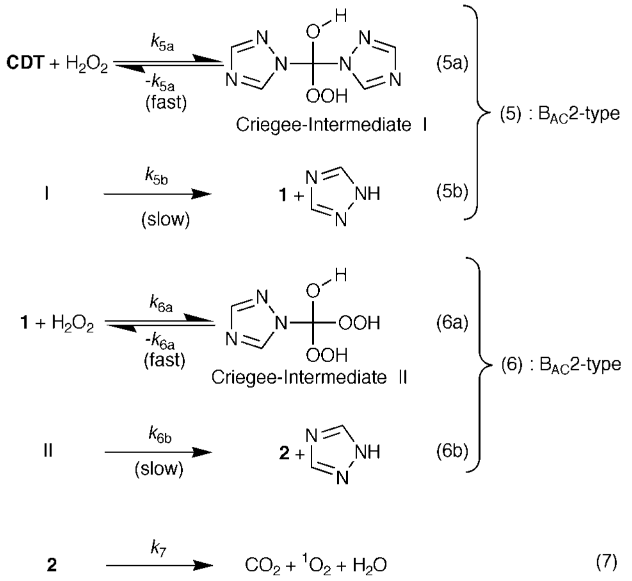
Fig. 3 Plots of ln k_5 and ln k_6 *versus* $1/T$ of the system CDT–H_2O_2 in THF; with $k_5 = k_f$ (CDT) and $k_6 = k_s$ (CDT) {see text}. Conditions: [CDT] = 1.25×10^{-2} mol dm^{-3}; [H_2O_2] = 1.25×10^{-1} mol dm^{-3}.

A.3 Temperature dependence of the second-order rate constants. Fig. 2 shows the $I_P(t)$→t curves observed for the system CDT–H_2O_2 as a function of temperature. The maximum of $I_P(t)$ increases and is shifted to shorter times with increasing temperature. The areas under the different curves are found to be equal within about 10%.

Measurements were performed in the temperature range between $T = 5$ °C and $T = 20$ °C. At temperatures $T > 20$ °C the reproducibility of the $I_P(t)$→t runs becomes worse. The Arrhenius plots of k_f(CDT) and k_s(CDT) are given in Fig. 3. From these plots the following values for the Arrhenius parameters are obtained: i) for the fast reaction, ln A_a(f) = 13 ± 3, E_{aa} (f) = 37 ± 5 kJ mol^{-1}; ii) for the slow reaction, ln A_a(s) = 10 ± 1,

E_{aa} (s) = 33 ± 3 kJ mol^{-1}; where A_a and E_{aa} denote apparent Arrhenius parameters (*vide infra*).

For both reaction (5) and reaction (6) relatively small values of the Arrhenius parameters are found. Especially from the small values of $A_a(f) \approx 4 \times 10^5$ dm^3 mol^{-1} s^{-1} and of $A_a(s) \approx 2 \times 10^4$ dm^3 mol^{-1} s^{-1} it can be deduced that in both reactions a preequilibrium takes place in which Criegee-intermediates are involved. The data are in accordance with the rule that the nucleophilic displacement by hydrogen peroxide at a carbonyl carbon atom is an addition–elimination process, which takes the form of a $B_{AC}2$-mechanism,[10] as outlined in Scheme 2.



Scheme 2

Moreover, in both reactions the second step (k_{5b} and k_{6b}, respectively) is rate determining, which is expected since in both reactions the leaving group (1,2,4-triazole) is more basic than the entering nucleophile (hydrogen peroxide).[10]

According to Scheme 2 the rate constants k_5 and k_6 are defined by eqns. (10) and (11), where K_{5a} and K_{6a} are the

$$k_5 = K_{5a}\,k_{5b} \qquad (10)$$

$$k_6 = K_{6a}\,k_{6b} \qquad (11)$$

constants of the preequilibria (5a) and (5b) and k_{5b} and k_{6b} denote the first-order rate constants of the decomposition of the corresponding Criegee-intermediates.

For reaction (6), *e.g.*, the Arrhenius equation (12) holds, where

$$k_6 = A_a(6) \exp\,[-E_{aa}(6)/RT] \qquad (12)$$

$A_a(6)$ and $E_{aa}(6)$ are defined by eqns. (13) and (14), where A(6b)

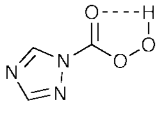
$$A_a(6) = A(6b) \exp\,[\Delta S°(6a)/R] \qquad (13)$$

$$E_{aa}(6) = \Delta H°(6a) + E_a(6b) \qquad (14)$$

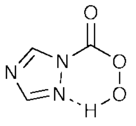
and E_a(6b) represent the Arrhenius parameters of reaction (6b) and $\Delta S°$ and $\Delta H°$ denote the reaction entropy and the reaction enthalpy, respectively, of equilibrium (6a).

Since the formation of the Criegee-intermediates is probably accompanied by negative values of $\Delta S°$ and $\Delta H°$ the low values of the Arrhenius parameters obtained are understandable.

A.4 Assignment of k_f and k_s. Now the question should be discussed which of the reactions (5) and (6) is the faster one. In this respect the results of the measurements carried out by Rebek *et al.*[2] are of interest. The authors have measured the epoxidation of cyclohexene by the system CDT–H_2O_2 in different solvents at T = 25 °C assuming that the peroxycarboxylic acid **1** is the epoxidizing agent. Surprisingly, the second-order rate constant "k_{ep}" determined by measuring the initial rates of epoxidation was found to be insensitive to solvent basicity, whereas in general for conventional peroxycarboxylic acids rates of epoxidation decrease as the Lewis basicity of the solvent increases. The values of "k_{ep}" determined in $CHCl_3$, THF and Et_2O are about 7.5×10^{-2} dm^3 mol^{-1} s^{-1}. This result is interpreted assuming that **1** does not react in the form **1a**, *i.e.* in a form generally postulated for conventional peroxycarboxylic acids,[11] but in the "more" stabilized form **1b**.



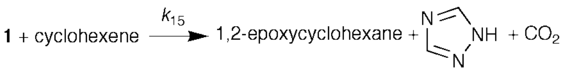
1a



1b

However this interpretation fails in so far as together with our results it can be deduced that the second-order rate constant "k_{ep}" determined by Rebek *et al.*[2] cannot be identical with k_{15}, the real rate constant of the epoxidation of cyclohexene by **1**.

As the authors report, at the beginning the epoxidation occurs according to a second-order reaction. This implies, if **1** is the real epoxidizing agent, that reaction (15) must occur much



(15)

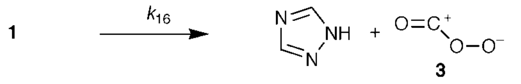
more quickly than reaction (6) (*vide infra*). Obviously, Rebek *et al.*[2] have measured the rate determining step of the epoxidation of cyclohexene. Thus the authors have determined the rate constant of reaction (5) which could be insensitive with respect to the Lewis basicity of the solvent. This reaction should be faster than reaction (6), since the carbonyl group of CDT may be more electronically activated and therefore more reactive towards hydrogen peroxide than that of **1**.

From the Arrhenius plots depicted in Fig. 3 for the rate constants k_f(CDT) and k_s(CDT) at T = 25 °C the values $k_f(CDT) = (1.3 \pm 0.5) \times 10^{-1}$ dm^3 mol^{-1} s^{-1} and $k_s(CDT) = (4.4 \pm 0.5) \times 10^{-2}$ dm^3 mol^{-1} s^{-1} are obtained. Within the error limits the value of k_f(CDT) agrees with the value of "k_{ep}"(THF) obtained by Rebek *et al.*[2] confirming the assumption that reaction (5) occurs faster than reaction (6). To test whether $k_f(CDT) = k_5$ is insensitive to the basicity of the solvents, we have performed measurements with the system CDT–H_2O_2 in $CHCl_3$ and Et_2O at 10 °C employing water free solutions of hydrogen peroxide in $CHCl_3$ and Et_2O, respectively. However in none of the systems $I_P(t)$ *versus t* curves were observed suitable for the evaluation of the rate constants k_f' and k_s', which probably results from the inhomogeneity caused by the water produced during the reaction of CDT with hydrogen peroxide.[12]

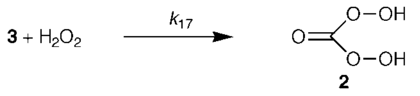
Nevertheless, if reaction (5) is the faster one then the equality $k_6 = k_s$(CDT) holds. With $k_6 = 4.4 \times 10^{-2}$ dm^3 mol^{-1} s^{-1} and the experimental conditions used by Rebek *et al.*[2] for the investigation of the epoxidation of cyclohexene: [cyclohexene] = 4.0×10^{-2} mol dm^{-3}; [CDT] = 8.0×10^{-2} mol dm^{-3} and $[H_2O_2] = 3.3 \times 10^{-1}$ mol dm^{-3} the rate constant k_{15} can be estimated according to the inequality k_{15} [**1**] [cyclohexene] $\gg k_6$ [**1**] $[H_2O_2] \Rightarrow k_{15} \gg k_6$ $[H_2O_2]$/[cyclohexene] and with $[H_2O_2] \approx [H_2O_2]_0 - [CDT] = 2.5 \times 10^{-1}$ mol dm^{-3} it follows that $k_{15} \gg (4.4 \times 10^{-2}) \times (2.5 \times 10^{-1})/4 \times 10^{-2} = 2.8 \times 10^{-1}$ dm^3 mol^{-1} s^{-1}, *i.e.* $k_{15} \approx 3 \times 10^0$ dm^3 mol^{-1} s^{-1}.

Up to now for peroxycarboxylic acids such a high value of a rate constant for olefin epoxidation in THF has not been observed. Values of this order of magnitude are known for epoxidation of olefins by dioxiranes as epoxidizing agents.[13]

Therefore it must be considered whether an epoxidizing agent other than **1** is involved. One possible hypothesis is to assume that **1** decomposes immediately after generation according to eqn. (16) to give, besides 1,2,4-triazole, carbon trioxide (CO_3) **3**, which could react in the absence of an olefin with hydrogen peroxide to give the diperoxycarbonic acid **2**. Obviously CO_3, which should exist in the dipolar structure[14] as described in eqn. (16), may be a powerful epoxidation agent comparable with dioxiranes.

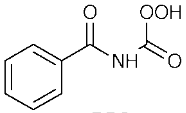


(16)



(17)

However the assumption that **1** is unstable and decomposes very fast into CO_3 and 1,2,4-triazole is based on the experience that the parent 1*H*-1,2,4-triazolecarboxylic acid is very unstable and decomposes immediately after formation into 1,2,4-triazole and CO_2.[1] But this conclusion is not compelling. In the case of the *N*-benzoylperoxycarbamic acid (BPC), first synthesized by



BPC

Höft and Ganschow,[4] the authors have shown that BPC is very stable at room temperature, whereas the parent *N*-benzoylcarbamic acid is very unstable at room temperature and decomposes immediately after generation into benzamide and CO_2.[4]

Moreover, the formation of CO_3 in the system CDT–H_2O_2 may not be compatible with the small difference observed for the second-order rate constants of the reactions (5) and (6) (*vide supra*). It can be assumed that the addition of hydrogen peroxide to CO_3 according to eqn. (17) will occur much more quickly than the nucleophilic displacement by hydrogen peroxide at the carbonyl atom of **1** and even of CDT, respectively. Consequently, if CO_3 is generated a greater difference between the rate constants of the consecutive second-order reaction could be expected. Thus the assumption made by Rebek *et al.*[2] that the peroxycarboxylic acid **1** is the epoxidizing agent appears to be most probable. Considering the value of $k_s'(\text{CDT}) = 3.4 \times 10^{-3}$ s^{-1} obtained under pseudo first-order conditions at $T = 10$ °C (see Fig. 1) for the lifetime of **1** a value of $\tau(\mathbf{1}) = 1/k_s' \approx 5$ min can be estimated indicating that **1** is more stable than its parent 1*H*-1,2,4-triazolecarboxylic acid.

To get more information about the *in situ* generated peroxy-intermediates in systems like CDT–H_2O_2 we have additionally studied the system 1*H*-1,2,4-triazolecarboxylic acid *p*-nitrophenyl ester (TCNP)–H_2O_2 in THF. In this system $^1O_2$ should be generated according to a mechanism discussed for CDT–H_2O_2.

B. Investigation of the system 1*H*-1,2,4-triazolecarboxylic acid *p*-nitrophenyl ester (TCNP)–H_2O_2

B.1 $^1O_2$ Phosphorescence intensity as a function of time. Fig. 4 shows a run of $I_P(t)$ *versus t* obtained under pseudo first-order conditions at $T = 20$ °C. The corresponding plot of ln $I_P(t)$ *versus t* is depicted in the inset of Fig. 4. The form of the $I_P(t)$ curve is consistent with the expectation that TCNP reacts with hydrogen peroxide in the same manner as CDT.

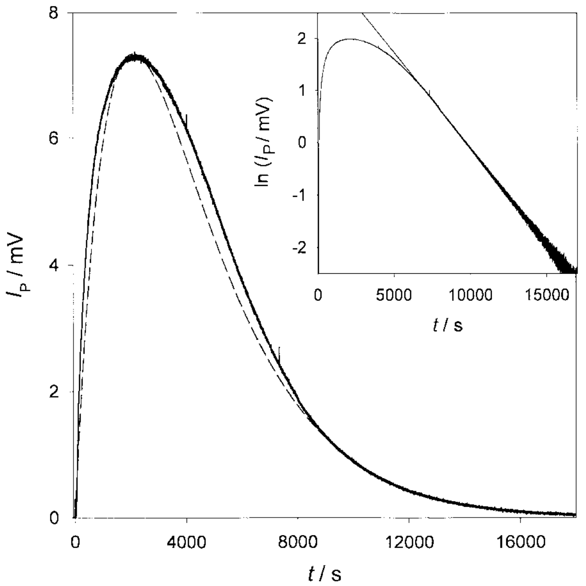


Fig. 4 $I_P(t)$ as a function of time of the system TCNP–H_2O_2 in THF. The inset shows the corresponding plot of ln $I_P(t)$ *versus* time. Conditions: [TCNP] = 5.2×10^{-2} mol dm^{-3}; [H_2O_2] = 5.2×10^{-1} mol dm^{-3}; $T = 20$ °C. —— = experimental curve; ---- = theoretically calculated curve according to eqn. (8) using $c_2 = (1.4 \pm 0.1) \times 10^{11}$ mV dm^3 s mol^{-1}; $k_p = (0.45 \pm 0.10)$ s^{-1} and $\tau_\Delta = (15 \pm 1)$ μs; $k_f'(\text{TCNP}) = 5.9 \times 10^{-4}$ s^{-1}; $k_s'(\text{TCNP}) = 3.7 \times 10^{-4}$ s^{-1}.

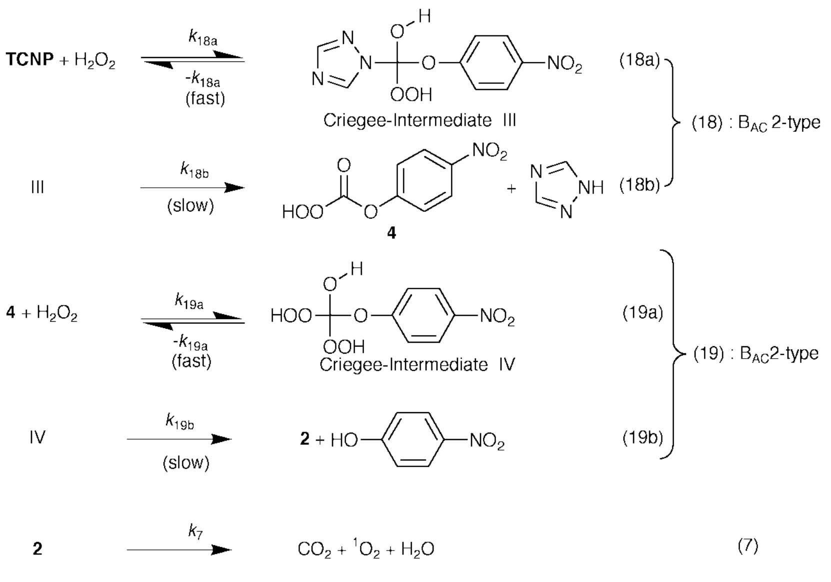
The pseudo first-order rate constants and the corresponding second-order rate constants of the slow reaction and the fast reaction, respectively, were found to be: $k_f'(\text{TCNP}) = (5.9 \pm 1.0) \times 10^{-4}$ s^{-1}, $k_f(\text{TCNP}) = (1.1 \pm 0.2) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}; $k_s'(\text{TCNP}) = (3.7 \pm 0.4) \times 10^{-4}$ s^{-1}, $k_s(\text{TCNP}) = (7.1 \pm 0.7) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}.

The value of k_f(TCNP) is by a factor of 100 smaller than that of $k_f(\text{CDT}) = 1.1 \times 10^{-1}$ dm^3 mol^{-1} s^{-1} obtained at $T = 20$ °C (see Fig. 3) and the value of k_s(TCNP) is also smaller than that of $k_s(\text{CDT}) = 3.7 \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, but only by a factor of about 50. It would appear that also in the system TCNP–H_2O_2 the first addition–elimination process occurs faster than the second one. Thus the difference in the rate constants indicates that the carbonyl group of CDT is more electronically activated than that of TCNP and moreover that the carbonyl group of the peroxycarboxylic acid **1** is also more activated than that of the peroxy acid generated in the system TCNP–H_2O_2 (*vide infra*).

The area under the experimental $I_P(t)$ curve amounts to $ar = (45350 \pm 4\%)$ mV s. With the values of c_2, k_p and τ_Δ given in the legend of Fig. 4 for the concentration of $^1O_2$ evolved a value of [$^1O_2$] = (4.8 ± 0.7) mol dm^{-3} is obtained. Within the error limits this value agrees very well with the initial concentration of [TCNP] = 5.2×10^{-2} mol dm^{-3} used in this experiment. This result distinctly shows that as observed for CDT–H_2O_2 in the system TCNP–H_2O_2 one molecule of TCNP yields one molecule of $^1O_2$ if pseudo first-order conditions are employed.

In Fig. 4 the theoretically evaluated $I_P(t)$-curve is also depicted. As already found for the system CDT–H_2O_2 the area under the theoretical curve is a little bit smaller than that of the experimental one. The difference between the areas only amounts to about 6%.

The experimental data found so far for the system TCNP–H_2O_2 are consistent with the following conclusions: i) in the first addition–elimination process 1,2,4-triazole should be eliminated, since this compound is less basic than the alternative leaving group (*p*-nitrophenyl anion); ii) consequently in this process *O*-*p*-nitrophenylmonoperoxycarbonic acid **4** should be formed (see Scheme 3); iii) for the lifetime of **4** a value of $\tau(\mathbf{4}) = 1/k_s'(\text{TCNP}) = 45$ min can be estimated. This value confirms the



Scheme 3

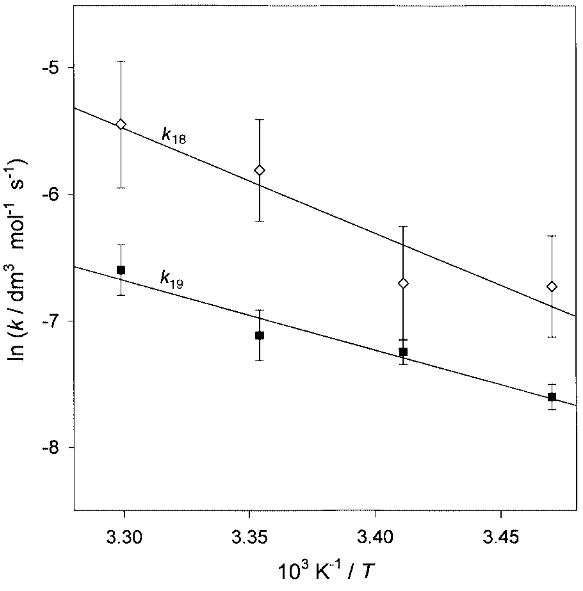


Fig. 5 Plots of ln k_{18} and ln k_{19} *versus* $1/T$ of the system TCNP–H_2O_2 in THF; with $k_{18} = k_f$(TCNP) and $k_{19} = k_s$(TCNP) {see text}. Conditions: [TCNP] = 5.2 × 10^{-2} mol dm^{-3}; [H_2O_2] = 5.2 × 10^{-1} mol dm^{-3}.

observation that *O*-arylmonoperoxycarbonic acids are more stable than the corresponding esters of the parent acid.[15]

In analogy to the system CDT–H_2O_2 for the formation of $^1O_2$ in the system TCNP–H_2O_2 the mechanism described in Scheme 3 can be presumed. This mechanism is confirmed by the results of the measurements at different temperatures.

B.2 Temperature dependence of the second-order rate constants. Measurements were performed between $T = 15$ °C and $T = 30$ °C. The Arrhenius plots of $k_{18} = k_f$(TCNP) and $k_{19} = k_s$(TCNP) are presented in Fig. 5. For the apparent Arrhenius parameters the following values were obtained: ln $A_a(18) = 22 \pm 7$, $E_{aa}(18) = (68 \pm 17)$ kJ mol^{-1}; ln $A_a(19) = 11 \pm 3$, $E_{aa}(19) = (46 \pm 7)$ kJ mol^{-1}.

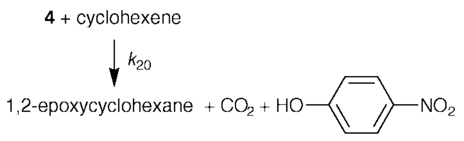
Again especially the low values of A_a found for reaction (18) and the slower reaction (19), respectively, indicate that in both reactions a preequilibrium between the educts and a Criegee-intermediate takes place according to a $B_{AC}2$-mechanism. Whereas the values of A_a obtained for the fast and slow reactions in the different systems agree very well within the error limits, the values of E_{aa} determined for reaction (19) and reaction (20) are distinctly greater than the corresponding E_{aa} values of reaction (5) and reaction (6), respectively. These results mean that the difference between the rate constants of the fast and the slow reaction observed in the different systems is mainly determined by the different E_{aa} values.

C. Miscellaneous measurements

C.1 Investigation of the system TCNP–H_2O_2 and CDT–H_2O_2 in the presence of cyclohexene. According to Schemes 1, 2 and 3 for both systems it is assumed that in the first addition–elimination process a reactive peroxycarboxylic acid is formed: **1** in the system CDT–H_2O_2 and **4** in the system TCNP–H_2O_2. **1** is found to be, by a factor of 50, more reactive towards hydrogen peroxide than **4**. Moreover, according to our evaluation **1** should be, by a factor of 50, more reactive towards cyclohexene than towards hydrogen peroxide. A similar behaviour with respect to the reactivity should also hold for **4**. To test this hypothesis we have carried out measurements with the system TCNP–H_2O_2 under pseudo first-order conditions in the presence of different concentrations of cyclohexene at $T = 20$ °C. The results are shown in Fig. 6.

Only for the lowest cyclohexene concentration of [cyclohexene] = [H_2O_2]/20 = 2.68 × 10^{-2} mol dm^{-3} a very small flat $I_P(t)$-signal is observed after adding hydrogen peroxide to the TCNP–cyclohexene solution. This signal increases very slowly but it increases considerably at about 500 s to a narrow I_P-signal. Moreover, it is found that the greater the cyclohexene concentration the smaller the signal and the later it is detected. At a cyclohexene concentration of [cyclohexene] = 2.68 × 10^{-1} mol dm^{-3} after about 1250 s a small I_P-signal is still observed. For equal concentrations of cyclohexene and hydrogen peroxide no I_P-signal can be detected.

In fact, these results confirm the expectation that **4** is more reactive towards cyclohexene (eqn. (20)) than towards hydrogen peroxide. The result that at equal concentrations of cyclohexene and hydrogen peroxide no $^1O_2$ can be detected distinctly demonstrates that **4** is practically completely consumed by the reaction with cyclohexene. The rate constant k_{20} for this reac-



(20)

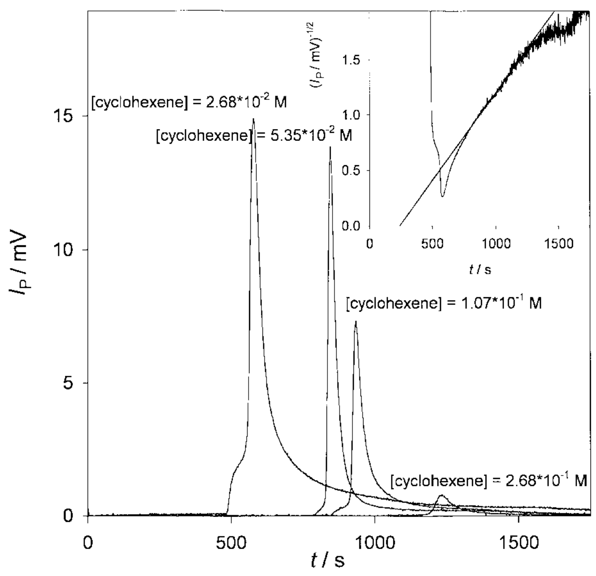


Fig. 6 $I_P(t)$ as a function of time of the system TCNP–cyclohexene–H_2O_2 in THF at different cyclohexene concentrations. The inset presents the plot of $1/\sqrt{I_P(t)}$ *versus* time {see text} for [cyclohexene] = 2.68×10^{-2} mol dm^{-3}. Conditions: [TCNP] = 5.35×10^{-2} mol dm^{-3}; [H_2O_2] = 5.35×10^{-1} mol dm^{-3}; T = 20 °C. M denotes the concentration in mol dm^{-3}.

tion can be approximately evaluated. For equal concentrations of TCNP and cyclohexene of 5.35×10^{-2} mol dm^{-3} and [H_2O_2] = 5.35×10^{-1} mol dm^{-3} (see legend of Fig. 6) $^1O_2$ formation is not observed within the first 800 s. From this result it can be deduced that within this time the following inequality holds:

$$k_{20} \gg \frac{k_{19}[H_2O_2]}{[\text{cyclohexene}]}$$

with $[H_2O_2] \approx [H_2O_2]_0 - [\text{TCNP}]$ and $k_{19} = 7.1 \times 10^{-4}$ dm^3 mol^{-1} s^{-1} one obtains

$$k_{20} \gg \frac{(7.1 \times 10^{-4}) \times (4.81 \times 10^{-1})}{5.35 \times 10^{-2}} = 6.4 \times 10^{-3}\,\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1}, \textit{i.e.}$$

$$k_{20} \approx 6 \times 10^{-2}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}.$$

Thus **4** is, by a factor of 50, less reactive towards cyclohexene than **1**, but in comparison with conventional peroxycarboxylic acids like peroxybenzoic acid **4** is about a factor of 100 more reactive.[2] In this respect it is interesting to recall the fact that **4** is about a factor of 50 less reactive towards hydrogen peroxide than **1**. Obviously the reactivity of **1** and **4** towards hydrogen peroxide runs parallel to the reactivity of both peroxycarboxylic acids towards cyclohexene.

With respect to the shape of the $I_P(t)$-signals shown in Fig. 6 it must be stated that the changes in $I_P(t)$ cannot be described exactly either by a first-order reaction or by a second-order reaction. For a second-order reaction a plot of $1/\sqrt{I_P(t)}$ *versus* time should give a straight line.[16] Such a plot of the first $I_P(t)$-signal is given in the inset of Fig. 6. From this plot it can be deduced that in the system TCNP–cyclohexene–H_2O_2, under the conditions used, a second-order reaction distinctly contributes to the overall formation of $^1O_2$ (*vide infra*).

In addition we have performed similar measurements with the system CDT–H_2O_2 at different cyclohexene concentrations in THF at T = 10 °C. Surprisingly this system exhibits different behaviour.

As shown in Fig. 7 for the lowest cyclohexene concentration of [cyclohexene] = [H_2O_2]/20 = 1.25×10^{-2} mol dm^{-3} (system (a)) about two seconds after addition of hydrogen peroxide an

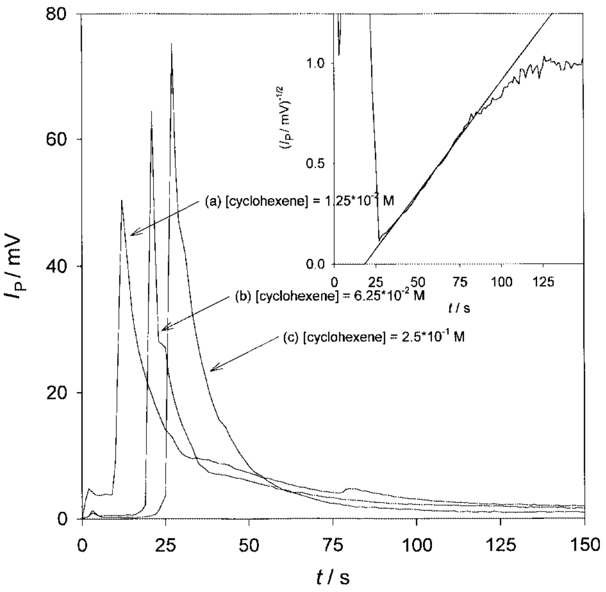


Fig. 7 $I_P(t)$ as a function of time of the system CDT–cyclohexene–H_2O_2 in THF at different cyclohexene concentrations. The inset shows the plot of $1/\sqrt{I_P(t)}$ *versus* time for the system (c). Conditions: [CDT] = 2.5×10^{-2} mol dm^{-3}; [H_2O_2] = 2.5×10^{-1} mol dm^{-3}; T = 10 °C. M denotes the concentration in mol dm^{-3}.

$I_P(t)$-signal of about 4 mV is observed which increases enormously at about 9 seconds. As observed for the system TCNP–cyclohexene–H_2O_2 the greater the cyclohexene concentration the longer the time at which the $I_P(t)$-signal is observed. But in contrast to the system TCNP–cyclohexene–H_2O_2 the height of the narrow $I_P(t)$-signal increases with increasing cyclohexene concentrations and at equal concentration of cyclohexene and hydrogen peroxide (system (c)) the highest $I_P(t)$-signal could be detected.

Moreover, the shape of the $I_P(t)$-signals can only be described by a second-order reaction as the straight line of the plot of $1/\sqrt{I_P(t)}$ *versus* time for the system (c) given in the inset of Fig. 7 demonstrates.

These results cannot be explained by the reaction mechanisms described so far. But it must be noted that they do not contradict the observation of Rebek *et al.*,[2] who found that 90% of cyclohexene is epoxidized by CDT–H_2O_2. The amounts of $^1O_2$ generated in both systems under the conditions employed are small (<4%) compared to the amounts expected for the systems investigated in the absence of cyclohexene.

In connection with the results presented in Figs. 6 and 7 the behaviour of the system CDI–H_2O_2 is of interest.

C.2 Investigation of the system *N*,*N′*-carbonyldiimidazole (CDI)–H_2O_2.

Measurements with the system CDI–H_2O_2 in THF carried out by Rebek *et al.*[2] have shown that this system is unsuitable for the epoxidation of cyclohexene. Only 1.5% 1,2-epoxycyclohexane was obtained. We have investigated this system under pseudo first-order conditions with [CDI] = 2.5×10^{-2} mol dm^{-3} and [H_2O_2] = 2.5×10^{-1} mol dm^{-3} at T = 10 °C. The result is given in Fig. 8.

Surprisingly, $^1O_2$ formation is observed. But the amount of $^1O_2$ is very small compared with the amount generated in the system CDT–H_2O_2 under the same conditions. However it is comparable to that of system (c) presented in Fig. 7. In addition the $I_P(t)$-signal is also consistent with a second-order reaction, which is evidently shown by the plot of $1/\sqrt{I_P(t)}$ *versus* t given in the inset of Fig. 8. It must be noted that neither in this case nor in the two cases discussed above can the second-order rate constant be evaluated, since neither the exact rate law nor the concentrations of the corresponding reacting compounds are known.

As already reported by Rebek *et al.*[2] in the system *N*,*N′*-

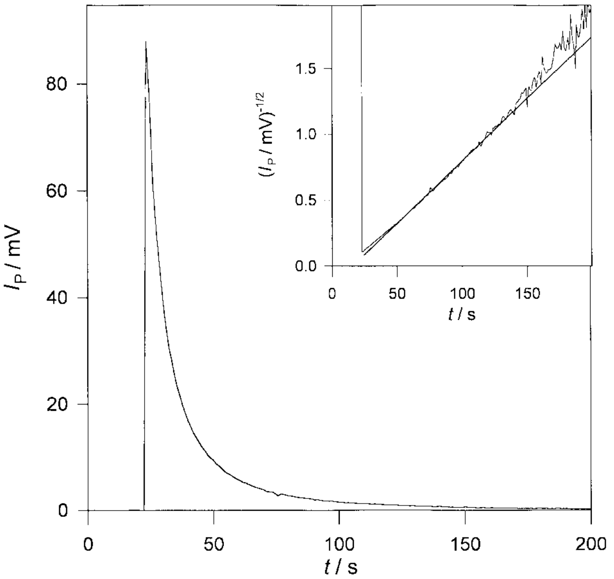
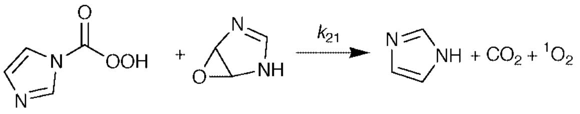


Fig. 8 $I_P(t)$ as a function of time of the system CDI–H_2O_2 in THF. The inset shows the corresponding plot of $1/\sqrt{I_P(t)}$ *versus* time. Conditions: [CDI] = 2.5 × 10^{-2} mol dm^{-3}; [H_2O_2] = 2.5 × 10^{-1} mol dm^{-3}; T = 10 °C.

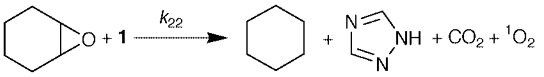
carbonyldi-2,4-dimethylpyrazole–H_2O_2 and in the system CDI–H_2O_2 coloured side products are developed. It can be assumed that in both systems in analogy to the system CDT–H_2O_2 in the first addition–elimination process a very reactive peroxycarboxylic acid is formed and that the corresponding acids can react with the azoles generated in the first process. The assumption that a reactive peroxycarboxylic acid can react for instance with imidazole is confirmed by the observation that the *in situ* generated peroxycarboxylic acid **1** reacts with imidazole. Addition of an excess of imidazole to the system CDT–H_2O_2 results immediately in the quenching of $^1O_2$ formation.

In contrast to 1,2,4-triazole both 2,4-dimethylpyrazole and imidazole contain a carbon–carbon double bond, which probably can be epoxidized by a reactive peroxycarboxylic acid. Assuming that among other things the epoxide can react further with the reactive peroxycarboxylic acid according to eqn. (21) the $I_P(t)$-signal observed for the system CDI–H_2O_2 can be explained.



(21)

This possibility has encouraged us to assume that 1,2-epoxycyclohexane produced in the systems TCNP–cyclohexene–H_2O_2 and CDT–cyclohexene–H_2O_2 could react with **4** and **1**, respectively, to give $^1O_2$ according to eqn. (22).



(22)

Attempts with the systems CDT–1,2-epoxycyclohexane–H_2O_2 and TCNP–1,2-epoxycyclohexane–H_2O_2 confirm this hypothesis. Fig. 9 shows for example the $I_P(t)$-signal observed for the system CDT–1,2-epoxycyclohexane–H_2O_2. In the inset the plot of $1/\sqrt{I_P(t)}$ *versus* t is given, which yields a straight line as expected for a second order reaction (see eqn. (22)).

However, it is evident that only a small amount of 1,2-epoxycyclohexane reacts with the *in situ* generated **1** to give $^1O_2$. The same observation is made for the system TCNP–1,2-epoxycyclohexane–H_2O_2. As yet we have no plausible explanation for these observations.

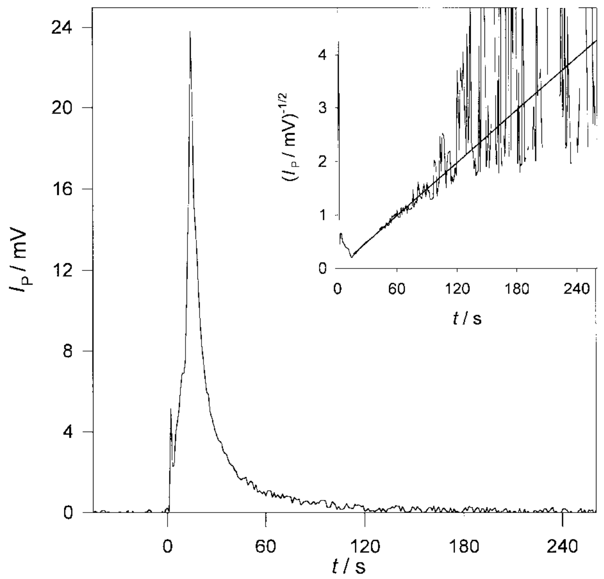


Fig. 9 $I_P(t)$ as a function of time of the system CDT–1,2-epoxycyclohexane–H_2O_2 in THF. The inset shows the corresponding plot of $1/\sqrt{I_P(t)}$ *versus* time. Conditions: [CDT] = 2.5 × 10^{-2} mol dm^{-3}; [1,2-epoxycyclohexane] = 2.5 × 10^{-1} mol dm^{-3}; [H_2O_2] = 2.5 × 10^{-1} mol dm^{-3}; T = 20 °C.

Apart from this the different behaviour observed for the systems CDT–cyclohexene–H_2O_2 and TCNP–cyclohexene–H_2O_2 (see Figs. 6 and 7) obviously reflects the different reactivity of the *in situ* generated peroxycarboxylic acids **1** and **4**. For both systems it can be deduced that in the presence of a large excess of cyclohexene compared to CDT and TCNP, respectively, and even at equal concentrations of cyclohexene and hydrogen peroxide the reactions between the peroxycarboxylic acids and hydrogen peroxide cannot compete with the corresponding epoxidation reactions. Moreover, for the system TCNP–cyclohexene–H_2O_2 this may hold also for the reaction between **4** and 1,2-epoxycyclohexane, whereas in the system CDT–cyclohexene–H_2O_2 the reaction between **1** and 1,2-epoxycyclohexane clearly can compete with the formation of 1,2-epoxycyclohexane. Consequently in the system CDT–cyclohexene–H_2O_2 the rate of the reaction between **1** and 1,2-epoxycyclohexane is high enough under the conditions used that $^1O_2$ generated in this reaction can be detected.[6]

The $I_P(t)$-signals of the system TCNP–cyclohexene–H_2O_2 observed at low cyclohexene concentrations can be explained by the contribution of two reactions to the overall $^1O_2$ formation, namely by the reaction between **4** and 1,2-epoxycyclohexane and by the reaction between **4** and hydrogen peroxide.

Further it should be noted that in contrast to **1** and **4** neither hydrogen peroxide (30%) nor conventional peroxycarboxylic acids like *m*-chloroperoxybenzoic acid react with 1,2-epoxycyclohexane to generate $^1O_2$.

Conclusions

The results of the investigation of the system CDT–H_2O_2 in THF are consistent with the assumption that in this system 1*H*-1,2,4-triazoleperoxycarboxylic acid **1** is formed as first postulated by Rebek *et al.*[2]

The results of the investigation of the system TCNP–H_2O_2 in THF are in accordance with the assumption that in this system *O*-*p*-nitrophenylmonoperoxycarbonic acid **4** is generated.

Both peroxycarboxylic acids are powerful epoxidizing agents. The reactivity of **1** towards olefins is comparable with that of dimethyldioxirane, *e.g.*, **1** is, by a factor of about ten thousand, more reactive towards cyclohexene than conventional peroxycarboxylic acids like peroxybenzoic acid. The reactivity of **4** towards olefins exceeds after all that of peroxybenzoic acid by a factor of one hundred.[2]

The disadvantage of the *in situ* generated peroxycarboxylic acids **1** and **4** is that they are also very reactive towards hydrogen peroxide. Thus in the case of less reactive olefins (*e.g.* dec-1-ene) this reaction successfully competes with the epoxidizing reaction resulting in a low efficiency of the formation of the epoxide desired.[2]

Whereas derivatives of the carbonic acid containing one hydroxy group are very unstable,[17] the lifetimes of **1** and **4** calculated under the pseudo first-order conditions demonstrate that both peroxycarboxylic acids (which contain a peroxy hydroxy group) are more stable than their parent carboxylic acids.

Acknowledgements

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