# On the formation of dioxiranes and of singlet oxygen by the ketone-catalysed decomposition of Caro's acid

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**Measurements of the infrared phosphorescence of singlet molecular oxygen ($^1O_2$) at 1270 nm have been used to demonstrate the formation of $^1O_2$ by the ketone-catalysed decomposition of peroxymonosulfuric acid (Caro's acid). The kinetics of the ketone-catalysed decomposition of Caro's acid have been studied by this technique and the rate law was found to be of first order for $HSO_5^-$, for ketone and for a pH-dependent factor $F = K_W/([H^+] + K_{a2})$. Eleven ketones were chosen to determine $k_{DI}$, the third-order rate constant for the formation of the corresponding dioxirane. The values of $k_{DI}$ depend on ketone structure and vary over a wide range. For both the acetone- and cyclohexanone-catalysed decomposition of Caro's acid measurements have been performed at different temperatures. The apparent activation energies $E_{aa}$ were determined to be $E_{aa}$(acetone) = 47.8 kJ mol$^{-1}$ and $E_{aa}$(cyclohexanone) = 36.0 kJ mol$^{-1}$, respectively. For the uncatalysed self-decomposition of Caro's acid the second-order rate constant was determined to be $k_2 = 5.9 \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$.**

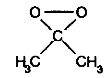
Peroxymonosulfuric acid (Caro's acid) decomposes spontaneously in aqueous solution into sulfuric acid and oxygen.[1,2] Two processes influence the stability of Caro's acid solutions: (*i*) the uncatalysed self-decomposition and (*ii*) the transition metal-catalysed decomposition. For the uncatalysed decomposition the rate law is of the form $v = k_2 [HSO_5^-][SO_5^{2-}]$ and accordingly this reaction can be regarded as a nucleophilic attack of the dianion of Caro's acid upon the peroxomonosulfate ion $HSO_5^-$(caroate).[1,3]

When transition metal catalysis is suppressed by adding a chelating agent such as ethylenediaminetetraacetate (EDTA), an essentially quantitative yield of molecular singlet oxygen ($^1O_2$) is obtained. This has been shown by Evans and Upton,[4] who studied the uncatalysed decomposition in the presence of the caesium salt of anthracene-9,10-bis(ethanesulfonate) as a trap for $^1O_2$.

Montgomery[5] observed in weak alkaline solutions that certain ketones significantly enhance the rate of the uncatalysed decomposition of Caro's acid. Small amounts of ketones decompose large quantities of caroate indicating the ketones' behaviour to be catalytic. The rate law was found to be of first order for the caroate, for the ketone and for $OH^-$: $v = k[HSO_5^-][\text{ketone}][OH^-]$. Furthermore, he discovered the 'oxidation power' of Caro's acid to be enhanced by ketones, suggesting a common intermediate should be involved. Also, it was suggested that this intermediate could be a dioxirane compound. Kinetic and $^{18}O$ labelling experiments performed by Edwards *et al.*[6] have provided powerful support for intermediary-generated dioxiranes in the ketone-catalysed decomposition of Caro's acid.

Later, Murray and Jeyaraman[7] isolated dimethyldioxirane **1** from a buffered aqueous solution containing caroate and acetone. Thereby, dimethyldioxirane was fully characterized by spectroscopic methods.[7,8] Other dioxiranes generated from the caroate–1,1,1-trifluoroacetone system[9] and the caroate–cyclohexanone system,[10] are described. Their potential as very powerful and versatile oxygen transfer reagents has been the subject of several excellent reviews.[11] More recently, a general and efficient protocol for the catalytic epoxidation of alkenes with caroate under biphasic reaction conditions has been developed by Denmark *et al.*[12]

According to the mechanism postulated by Edwards *et al.*,[6] the dianion of Caro's acid attacks the dioxirane to generate oxygen (*vide infra*). On spin-conservation grounds $^1O_2$ should be produced rather than $^3O_2$. Accordingly, in this paper the ketone-catalysed decomposition of Caro's acid has been studied by measuring the $^1O_2$ phosphorescence emission at $\lambda$ = 1270 nm for the direct detection of $^1O_2$. Also, for comparison the uncatalysed decomposition has been examined by this technique.



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## Experimental

### Materials

The source of potassium peroxomonosulfate (caroate) was the triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ (Fluka), used as received. The solvent was twice-distilled water. The reactions were carried out in buffer solutions in the presence of a polyphosphonate chelating agent, Dequest 2066 (Monsanto), which was kindly donated by Hoechst AG, Frankfurt. In the pH region 8.0–8.5 sodium dihydrogenphosphate (Merck, Suprapur) was used, from pH 9.0–11.0 sodium hydrogencarbonate (Merck, pa), from pH 11.0–12.0, disodium hydrogenphosphate (Merck, Suprapur) and aqueous sodium hydroxide 30% (Merck, Suprapur). For comparison we used in the pH region 9.4–10.0 sodium tetraborate (Fluka, pa). The pH measurements were performed using a WTW pH 525 model pH-meter. Acetone (Aldrich, HPLC grade), butan-2-one (Aldrich, pa), pentan-3-one (Fluka, pa), 3,3-dimethylbutan-2-one (pinacolone; Aldrich, pa), cycloheptanone (Aldrich, pa) and cyclohexanone (Fluka, pa) were distilled from dry potassium carbonate prior to use and stored over 4 Å molecular sieves. 2-Acetylpyridine (Aldrich, pa), di-2-pyridyl ketone (Aldrich, pa), fluoroacetone (Aldrich, pa) and 1,1,1-trifluoroacetone (Fluka, purum) were of the highest purity and used as received. *N*,*N*-Dimethyl-4-oxopiperidinium nitrate was synthesized by the literature procedure[13] followed by anionic exchange of the requisite iodide salt with silver nitrate.[12] The purity was confirmed by $^1H$ and $^{13}C$ NMR spectroscopy. In the measurements of the yield of $^1O_2$ the potassium peroxomonosulfate was added to the thermostatted buffer solution containing acetone. After suitable time intervals the peroxy acid content was analysed iodometrically by titration with 0.1 mol dm$^{-3}$ sodium thiosulfate (Riedel-de-Haen).

### Singlet oxygen infrared emission measurements

The near-infrared luminescence (IRL)-spectrometer used in our studies for recording the $^1O_2$ phosphorescence emission at $\lambda$ = 1270 nm has been described in detail.[14–16]

For the intensity of the $^1O_2$ phosphorescence emission, $I_p$, eqn. (1) holds,[16] where $c = 2.6 \times 10^8$ V dm$^3$ mol$^{-1}$ s is a

$$I_p = ck_p\tau_\Delta d[^1O_2]/dt \qquad (1)$$

constant of the IRL-spectrometer,[16] $k_p$ is the rate constant of the $^1O_2$ phosphorescence emission (in water: $k_p = 0.18$ s$^{-1}$)[17] and $\tau_\Delta$ is the lifetime of $^1O_2$ (in water: $\tau_\Delta = 4.2$ μs).[18] $d[^1O_2]/dt$ denotes the rate of $^1O_2$ formation.

Reactions were carried out in thermostatted 1 cm quartz cuvettes. To the buffer/Dequest 2066/ketone solutions the triple salt was added in solid form, dissolving within a few seconds. Vigorous stirring was necessary. The initial concentrations of Caro's acid were in the range $2.2 \times 10^{-3}$ to $2.0 \times 10^{-2}$ mol dm$^{-3}$. For evaluation of the rate constant, values of $I_p(t)$ measured at 0.5 min $\leqslant t \leqslant$ 10 min were taken into account.

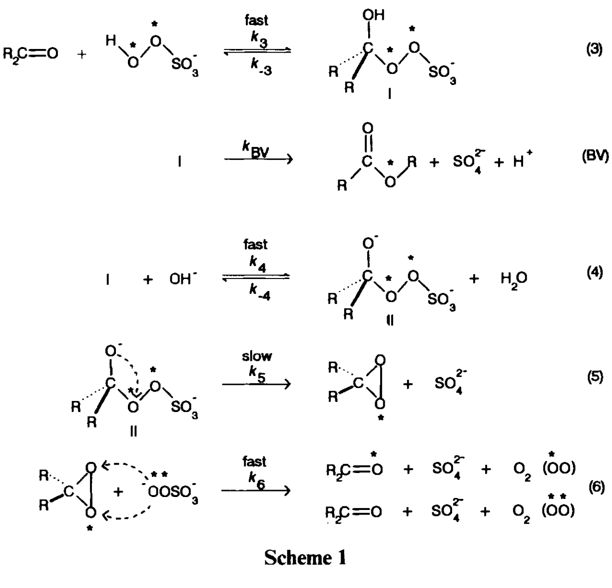
### Rate law and expression for $I_p$ of the ketone-catalysed decomposition

The self-decomposition of Caro's acid [eqn. (2)] forming $^1O_2$

$$HSO_5^- + SO_5^{2-} \xrightarrow{k_2} HSO_4^- + SO_4^{2-} + {}^1O_2 \qquad (2)$$

occurs as a competitive reaction involving ketone-catalysed decomposition. Starting with low caroate concentration this undesired consumption of the caroate is negligible and keeps the caroate concentration low during investigations of the ketone-catalysed decomposition of Caro's acid.

Scheme 1 shows the mechanism of the ketone-catalysed decomposition postulated by Edwards *et al.*[6] According to this mechanism the oxygen gas evolved should retain 75% of $^{18}O$ when starting with caroate doubly labelled at the peroxide bond; the experimental finding was (73 ± 2)%. Obviously, this key experiment has opened a door on dioxirane chemistry.



Scheme 1

Generally, the side reaction involving Baeyer–Villiger oxidation[19] of the ketone [Scheme 1, path (BV)] is negligible with most ketones employed (*e.g.* acetone, 1,1,1-trifluoroacetone, *N*,*N*-dimethyl-4-oxopiperidinium nitrate). However, a significant loss (about 20%) of ketone is observed using cyclohexanone as catalyst at pH 9.[5,20] The rate law firstly determined by Montgomery[5] can be written in the form eqn. (7), where $[HSO_5^-]_T$ denotes the total concentration of

$$-\frac{1}{2}\frac{d[HSO_5^-]_T}{dt} = k_{obs}[HSO_5^-]_T \qquad (7)$$

caroate. On the basis of the mechanism given in Scheme 1, $k_{obs}$ is defined as eqn. (8), where $K_3$ and $K_4$ are the constants of the

$$k_{obs} = K_3K_4k_5[\text{ketone}]F \qquad (8)$$

equilibria (3) and (4) and $k_5$ is the first-order rate constant for the rate determining step of the formation of the reactive dioxirane from the intermediate **II**. The factor $F$ is defined as eqn. (9), where $K_W$ is the ionic product of water and $K_{a2}$ =

$$F = \frac{K_W}{([H^+] + K_{a2})} \qquad (9)$$

$3.98 \times 10^{-10}$ mol dm$^{-3}$ is the second dissociation constant of Caro's acid.

Preliminary tests have shown that in step (6) $^1O_2$ is produced (*vide infra*). For the rate of the $^1O_2$ formation eqn. (10) holds.

$$\frac{d[^1O_2]}{dt} = -\frac{1}{2}\frac{d[HSO_5^-]_T}{dt} = k_{obs}[HSO_5^-]_T \qquad (10)$$

For constant ketone concentration and constant value of $F$ integration of (10) resulted in eqn. (11), where $[HSO_5^-]_T(0)$ denotes the total concentration of caroate at time $t = 0$. Introduction of eqn. (11) into eqn. (10) for $I_p(t)$ gives eqn. (12), where $I_p(0)$ is the phosphorescence intensity at time $t = 0$, eqn. (13).

$$[HSO_5^-]_T(t) = [HSO_5^-]_T(0)\exp[-2k_{obs}t] \qquad (11)$$

$$I_p(t) = I_p(0)\exp[-2k_{obs}t] \qquad (12)$$

$$I_p(0) = ck_p\tau_\Delta k_{obs}[HSO_5^-]_T(0) \qquad (13)$$

### Rate law and expression for $I_p$ of the uncatalysed decomposition

The rate law for the $^1O_2$ formation of the uncatalysed decomposition of Caro's acid is of the form eqn. (14) where $k_2$ is

$$\frac{d[^1O_2]}{dt} = -\frac{1}{2}\frac{d[HSO_5^-]_T}{dt} = k_2F'[HSO_5^-]_T^2 \qquad (14)$$

the second-order rate constant and $F'$ is defined as eqn. (15).

$$F' = \frac{[H^+]}{K_{a2}(1 + [H^+]/K_{a2})^2} \qquad (15)$$

For the intensity of the $^1O_2$ phosphorescence emission at time $t$ eqn. (16) can be deduced.

$$I_p(t) = ck_p\tau_\Delta k_2F'[HSO_5^-]_T(0)\frac{1}{[1 + 2k_2F'[HSO_5^-]_T^2(0)t]^2} \qquad (16)$$

## Results and discussion

Preliminary tests of the acetone-catalysed decomposition of Caro's acid with the IRL-technique have unequivocally shown that $^1O_2$ is generated in this reaction, as demonstrated by measurements of its infrared phosphorescence spectrum (Fig.

1). In this connection it should be noted that for the uncatalysed decomposition under the same conditions due to the lower $^1O_2$ phosphorescence intensity no phosphorescence spectrum could be recorded.

In order to verify eqns. (12) and (13) and the results reported by Montgomery[5] and Edwards *et al.*[6] the following measurements were conducted.

### $^1O_2$ Phosphorescence intensity as a function of time

From eqn. (12) it can be deduced that a plot of $I_p(t)$ *versus* time resulted in a monoexponential decay. Fig. 2 shows such a plot for the acetone-catalysed decomposition of Caro's acid. The plot of ln $I_p(t)$ *versus* time resulted in a straight line with a slope equal to $-2k_{obs}$. It is linear through four half-lives, *i.e.* practically through the whole reaction time indicating that the time dependence of $I_p(t)$ is exactly described by eqn. (12). Similar plots have also been observed for the other ketones. For cyclohexanone, plots of ln $I_p(t)$ *versus* time were found to be linear for two half-lives but not for the entire reaction time. This is due to the fact that during reaction a significant consumption of cyclohexanone takes place.[5,20]

### $^1O_2$ Phosphorescence intensity $I_p$ as a function of $[HSO_5^-]_T(0)$, [ketone] and the factor $F$

According to eqn. (13) the $^1O_2$-phosphorescence intensity at time zero $I_p(0)$ is directly proportional to the initial caroate concentration $[HSO_5^-]_T(0)$. With acetone as catalyst, measurements were performed at constant pH and constant ketone concentration at different concentrations of $[HSO_5^-]_T(0)$. The linear regression of log $I_p(0)$ *versus* log $[HSO_5^-]_T(0)$ yields a straight line and the gradient of this plot is (1.00 ± 0.05) in agreement with expectation (Fig. 3). The reaction is first order in $[HSO_5^-]_T(0)$ up to $1.0 \times 10^{-2}$ mol dm$^{-3}$ at pH 11.0.

This was confirmed at pH 10.0 only up to $6.0 \times 10^{-3}$ mol dm$^{-3}$. The reason for this restriction is the self-decomposition [eqn. (2)] of Caro's acid for pH values close to $pK_{a2}$. Accordingly, $^1O_2$ was detected only with caroate itself in the absence of ketone at concentrations higher than $6.0 \times 10^{-3}$ mol dm$^{-3}$ and at pH 10.0. Analogously, we investigated the catalytic decomposition of Caro's acid by ketones at low concentration of peroxomonosulfate where the self-decomposition is negligible.

According to eqn. (8) the pseudo first-order rate constant $k_{obs}$ is directly proportional to both the ketone concentration and the factor $F$. Variations in ketone concentration were performed with acetone as catalyst. The caroate concentration and the factor $F$ were held constant at $4.0 \times 10^{-3}$ mol dm$^{-3}$ and pH 10.0, respectively. Fig. 4 shows the plot of log $k_{obs}$ *versus* log [acetone] in the acetone-catalysed decomposition of Caro's acid.

The slope of the straight line is found to be (0.98 ± 0.02). Similar results are obtained at $8.0 \leqslant \text{pH} \leqslant 12.0$. For the other ketones the plots of log $k_{obs}$ *versus* log [ketone] at pH 10.0 yield a gradient (1.00 ± 0.06), confirming that the loss of Caro's acid and with it the formation of $^1O_2$ are actually first-order in ketone concentration. Also, the reaction order of $d[^1O_2]/dt$ with respect to acetone is determined by measuring $I_p(0)$ as a function of [acetone]. Measurements were performed at pH 10.0 and $[HSO_5^-]_T(0) = 4.0 \times 10^{-3}$ mol dm$^{-3}$ in the range 6.81–135 mmol dm$^{-3}$ of acetone. Under these conditions eqn. (17) deduced from eqns. (8) and (13) should hold true.

$$I_p(0) = ck_p\tau_\Delta K_3K_4k_5\, 8.0 \times 10^{-8}\,[\text{acetone}] \qquad (17)$$

In order to determine the exponent of [acetone] a double logarithmic plot of $I_p(0)$ *versus* [acetone] was conducted. The slope of the straight line was found to be (1.05 ± 0.06) indicating that $d[^1O_2]/dt$ is actually first order with respect to acetone.

The acetone-catalysed decomposition of Caro's acid was also

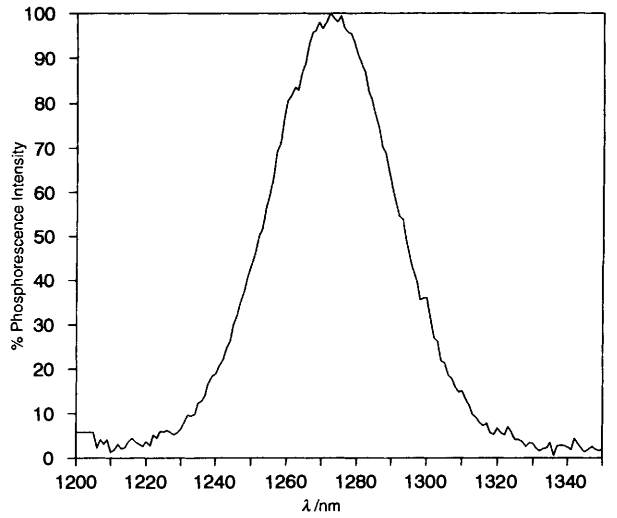


**Fig. 1** Phosphorescence spectrum of $^1O_2$ ($^1\Delta_g$, $v = 0 \rightarrow {}^3\Sigma_g^-$, $v = 0$) for the acetone-catalysed decomposition of Caro's acid. Conditions: $[HSO_5^-]_T(0) = 1.0 \times 10^{-2}$ mol dm$^{-3}$, [acetone] = $1.35 \times 10^{-1}$ mol dm$^{-3}$, [Dequest] = $1.0 \times 10^{-4}$ mol dm$^{-3}$, pH = 11.0, $T$ = 25 °C, half-bandwidth of emission monochromator, $\lambda_{\frac{1}{2}}$ = 34 nm.

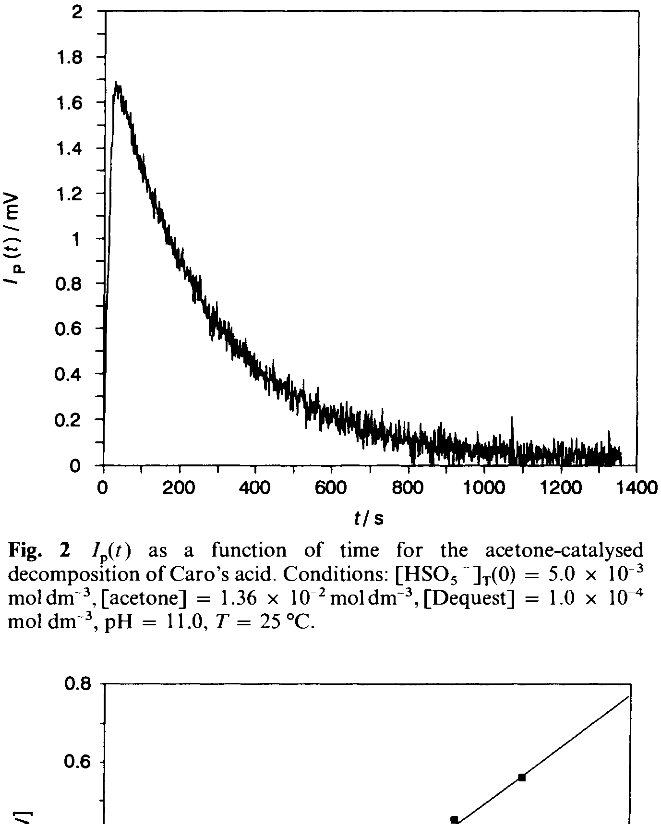


**Fig. 2** $I_p(t)$ as a function of time for the acetone-catalysed decomposition of Caro's acid. Conditions: $[HSO_5^-]_T(0) = 5.0 \times 10^{-3}$ mol dm$^{-3}$, [acetone] = $1.36 \times 10^{-2}$ mol dm$^{-3}$, [Dequest] = $1.0 \times 10^{-4}$ mol dm$^{-3}$, pH = 11.0, $T$ = 25 °C.

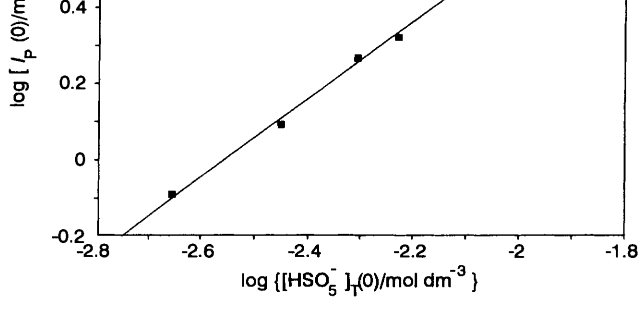


**Fig. 3** Double logarithmic plot of $I_p(0)$ *versus* $[HSO_5^-]_T(0)$ for the acetone-catalysed decomposition of Caro's acid. Conditions: [acetone] = $1.36 \times 10^{-2}$ mol dm$^{-3}$, [Dequest] = $1.0 \times 10^{-4}$ mol dm$^{-3}$, pH = 11.0, $T$ = 25 °C.

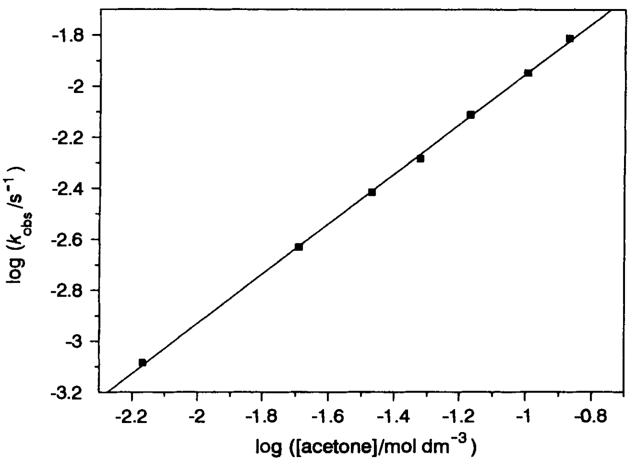


**Fig. 4** Double logarithmic plot of $k_{obs}$ *versus* [acetone] for the acetone-catalysed decomposition of Caro's acid. Conditions: $[HSO_5^-]_T(0) = 4.0 \times 10^{-3}$ mol dm$^{-3}$, [Dequest] = $1.0 \times 10^{-4}$ mol dm$^{-3}$, pH = 10.0, $T = 25$ °C.

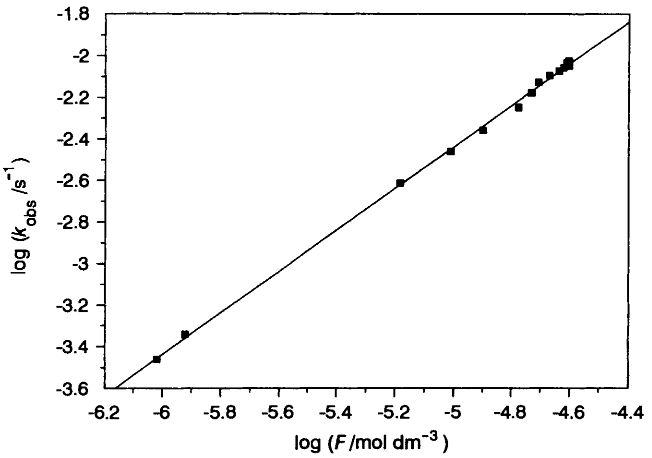


**Fig. 5** Double logarithmic plot of $k_{obs}$ *versus* $F$ for the acetone-catalysed decomposition of Caro's acid. Conditions: $[HSO_5^-]_T(0) = 5.0 \times 10^{-3}$ mol dm$^{-3}$, [acetone] = $6.78 \times 10^{-2}$ mol dm$^{-3}$, [Dequest] = $1.0 \times 10^{-4}$ mol dm$^{-3}$, $T = 25$ °C.

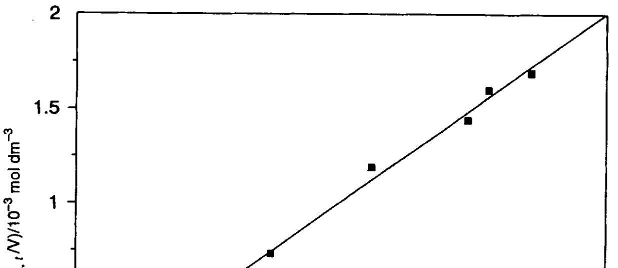


**Fig. 6** Plot of $n_{\Delta,t}/V$ *versus* $[HSO_5^-]_T(0) - [HSO_5^-]_T(t)$ for the acetone-catalysed decomposition of Caro's acid. Conditions: $[HSO_5^-]_T(0) = 5.0 \times 10^{-3}$ mol dm$^{-3}$, [acetone] = $4.07 \times 10^{-2}$ mol dm$^{-3}$, [Dequest] = $1.0 \times 10^{-4}$ mol dm$^{-3}$, pH = 10.0, $T = 25$ °C.

studied as a function of pH. The wide pH range required the use of more than one type of buffer mixture (*vide supra*). Although the existence of peroxocarbonate species in aqueous $H_2O_2$ solution have been mentioned[21] there are no reports of interference from carbonate buffers and phosphate buffers, respectively, in peroxide reactions. The investigation of the pH dependence of the acetone-catalysed decomposition of Caro's acid shows that $k_{obs}$ rises with increasing pH, especially in the pH range 8–10.† At pH 10.5 the pseudo first-order constant $k_{obs}$ reaches a maximum value above which the rate is approximately constant.

Fig. 5 shows the plot of log $k_{obs}$ *versus* log $F$. The straight line with the slope (1.00 ± 0.02) indicates that, according to eqn. (8), $k_{obs}$ is directly proportional to $F = K_W/([H^+] + K_{a2})$.

At first sight, this result is in contrast to the findings obtained for the cyclohexanone-catalysed decomposition of Caro's acid.[5] Montgomery's plot of log $k_{obs}$ *versus* pH did not result in a curve of slope 1. This is due to his suggestion that $k_{obs}$ is directly proportional to the $OH^-$ concentration in the range $7 \leqslant pH \leqslant 12.5$. However, as shown in Fig. 5, $k_{obs}$ is directly proportional to the factor $F$. Whereas the $OH^-$ concentration increases proportionally with increasing pH, the factor $F = 10^{-14}/([H^+] + 3.98 \times 10^{-10})$ mol dm$^{-3}$ reaches a limiting value. At pH 11, $F$ amounts to $10^{-5}$ mol dm$^{-3}$, whereas at this pH the $OH^-$ concentration is $10^{-3}$ mol dm$^{-3}$.

The cyclohexanone-catalysed decomposition of Caro's acid was also measured under the same conditions as performed by Montgomery with $[HSO_5^-]_T(0) = 2.7 \times 10^{-3}$ mol dm$^{-3}$ and [cyclohexanone] = $10^{-2}$ mol dm$^{-3}$ at $T = 28$ °C. The values of $k_{obs}$ obtained in the range $8 \leqslant pH \leqslant 12$ are in excellent agreement within the error limits with the values of $k_{obs}$ reported by Montgomery.[5] The linear regression analysis of log $k_{obs}$ *versus* log $F$ for cyclohexanone as catalyst leads to a value of (0.97 ± 0.03) for the slope supporting the data found for acetone as catalyst and confirming that the loss of $HSO_5^-$ ion and with it the formation of $^1O_2$ is first order in the factor $F$ as predicted by eqn. (8) and not first order in $OH^-$ concentration and pH, respectively.

**Yield of $^1O_2$ formation ($Y_{^1O_2}$)**

According to eqn. (18) Evans and Upton[4] obtained for $Y_{^1O_2}$ a value of 0.5, indicating the formation of one $^1O_2$ molecule per two molecules of $HSO_5^-$. Also, for the ketone-catalysed decomposition the stoichiometric balance should hold true. $Y_{^1O_2}$ is given by eqn. (19), where $n_{\Delta,t}$ denotes the total number of

$$2\,HSO_5^- \longrightarrow 2\,HSO_4^- + {}^1O_2 \qquad (18)$$

$$Y_{^1O_2} = \frac{n_{\Delta,t}/V}{[HSO_5^-]_T(0) - [HSO_5^-]_T(t)} \qquad (19)$$

moles of $^1O_2$ formed at the time $t$, $V$ is the sample volume and $[HSO_5^-]_T(0) - [HSO_5^-]_T(t)$ represents the concentration loss of $[HSO_5^-]_T$ at time $t$. $n_{\Delta,t}/V$ was determined as previously described[16] and the loss of $[HSO_5^-]_T$ was determined by iodometric titration at five different times.

Fig. 6 shows the plot $n_{\Delta,t}/V$ *versus* $[HSO_5^-]_T(0) - [HSO_5^-]_T(t)$ determined for the acetone-catalysed decomposition of Caro's acid. The slope of the straight line is SL = $Y_{^1O_2}$ = 0.50 ± 0.03 indicating that the evolved oxygen is formed quantitatively as $^1O_2$.

**Third-order rate constants for the formation of dioxiranes**

The third-order rate constants for the formation of the dioxiranes, $k_{DI}$, of eleven ketones investigated at $T = 25$ °C are summarized in Table 1.

For the fluoroacetone- and 1,1,1-trifluoroacetone-catalysed decomposition of Caro's acid a temperature of $T = 10$ °C was

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† We have investigated the effect of the borate buffer compared to the hydrogencarbonate buffer under the same ionic strength at constant pH and $T = 25$ °C. Interestingly, the resulting first-order rate constant $k_{obs}$ is about a factor 2.5 lower in borate buffers than in hydrogencarbonate buffers.

**Table 1** Third-order rate constants for the formation of the dioxiranes for the ketone-catalysed decomposition of Caro's acid[a]

| Entry | Ketone | $k_{DI} = K_3K_4k_5$/ dm$^6$ mol$^{-2}$ s$^{-1}$ | $\frac{k_{DI}(\text{ketone})}{k_{DI}(\text{acetone})}$ |
|---|---|---|---|
| 1 | Acetone | $(5.7 \pm 0.1) \times 10^3$ | 1.0 |
| | | $(2.1 \pm 0.1) \times 10^{3\,b}$ | |
| 2 | Butan-2-one | $(3.6 \pm 0.1) \times 10^3$ | 0.63 |
| 3 | Pentan-3-one | $(1.4 \pm 0.2) \times 10^3$ | 0.25 |
| 4 | Pinacolone | $(3.5 \pm 0.2) \times 10^2$ | 0.06 |
| 5 | 2-Acetylpyridine | $(1.4 \pm 0.2) \times 10^4$ | 2.5 |
| 6 | Di-2-pyridyl ketone | $(1.0 \pm 0.1) \times 10^5$ | 17.5 |
| 7 | Fluoroacetone | $(1.1 \pm 0.1) \times 10^{5\,b}$ | 52 |
| 8 | 1,1,1-Trifluoroacetone | $(1.0 \pm 0.3) \times 10^{5\,b}$ | 48 |
| 9 | Cycloheptanone | $(1.4 \pm 0.2) \times 10^3$ | 0.25 |
| 10 | Cyclohexanone | $(5.6 \pm 0.1) \times 10^4$ | 9.8 |
| | | $(7.2 \pm 0.2) \times 10^{4\,c}$ | |
| 11 | *N*,*N*-Dimethyl-4-oxo-piperidinium nitrate | $(3.5 \pm 0.1) \times 10^6$ | 614 |
| | | | 1050[d] |

[a] At 25 °C in a pH 10.0 (hydrogencarbonate) buffer unless stated otherwise. [b] $T = 10$ °C, see text. [c] $T = 28$ °C. [d] In a pH 9.0 (hydrogencarbonate) buffer.

chosen due to the high volatility of the fluoroketones. Also, for comparison the acetone-catalysed decomposition of peroxomonosulfate was performed at $T = 10$ °C. For pinacolone, we corroborated the ratio $k_{DI}$(pinacolone):$k_{DI}$(acetone) in an analogous $D_2O$ buffer because of the increased lifetime of $^1O_2$ in $D_2O$ compared to $H_2O$. According to eqn. (8) the values of $k_{DI}$ at pH 10.0 were calculated from the slope of $k_{obs}$ *versus* [ketone].

For acyclic ketones with a bulky group in the α-position a significant decrease in $k_{DI}$ is observed in the order pinacolone < pentan-3-one < butan-2-one < acetone (entries 1-4). As an example, the *tert*-butyl group in pinacolone significantly diminished the rate of dioxirane formation compared to acetone. This is the order of reactivity reported for the epoxidation of (*E*)-6-(phenylmethoxy)hex-2-ene in caroate–ketone mixtures.[12] The epoxide yield decreases with increasing α-substitution in the range: acetone (87%) > butan-2-one (40%) > pentan-3-one (5%). The substitution at the carbon next to the carbonyl group leads to a significant decrease in the equilibrium constant $K_3$ for the formation of the tetrahedral intermediate **I**.[11c] The decrease in $k_{DI}$ is not affected by $k_{BV}$, though the migration of different groups in the Baeyer–Villiger reaction was found to be in the order *tert*-alkyl > *sec*-alkyl > *n*-alkyl > methyl.[22]

Apart from the steric interaction on $k_{DI}$, an electronic contribution also has to be taken into account. With increasing electrophilicity of the ketone, $k_{DI}$ increases compared to acetone (entries 1, 5–8). This is shown for the rate of formation of dioxirane, where the fluoroketones have a higher rate of a factor 50 compared to acetone as reference. Again, an electron-withdrawing substituent at the carbonyl carbon leads to an increased equilibrium constant $K_3$. This was demonstrated for the analogous reaction between hydrogen peroxide and acetone.[23] The low equilibrium constant value for formation of 2-hydroxy-2-hydroperoxypropane ($K = 0.086$ dm$^3$ mol$^{-1}$, $T =$ 25 °C) as compared with the equilibrium constant for formation of the analogous adduct from acetaldehyde and hydrogen peroxide ($K = 48$ dm$^3$ mol$^{-1}$)[24] was attributed to the electron deficiency at the carbonyl carbon of the acetaldehyde. It is remarkable that the ratio $k_{DI}$(1,1,1-trifluoroacetone):$k_{DI}$(acetone) given in the second column of Table 1 does not correlate with the oxidation strength of the isolated dioxiranes. Recently, oxidations of different compounds were performed using dimethyldioxirane **1** and methyltrifluoromethyldioxirane (MTFD). For the ratio of the second-order rate constants $k_{ox}$(MTFD):$k_{ox}$ (**1**) in the oxidation of cumene[9b] and of silanes,[25] respectively, a value of 600 was found. This value is by a factor of 12 higher than that determined for the ratio $k_{DI}$(1,1,1-trifluoroacetone):$k_{DI}$(acetone), indicating the difference between the rate of formation of dioxirane in the ketone-catalysed decomposition of Caro's acid in aqueous solution and the reactivity of isolated dioxiranes toward substrates in organic solvents. The lower catalytic activity of the fluoroketones in aqueous solution is due to the hydration of these ketones. Increasing electronegativity of the substituents at the carbonyl carbon increases the tendency for hydration of ketones.[26] The loss of reactivity in aqueous solution could be explained by the slow exchange between the OH in the hydrate and the attacking peroxomonosulfate.[12]

Also, the pyridine group leads to an enhanced decomposition of Caro's acid compared to acetone. The ratio $k_{DI}$(di-2-pyridyl ketone):$k_{DI}$(2-acetylpyridine) is in good agreement with the findings of the relative $k_{ox}$ values for the bleaching of the anionic dye Polar Brilliant Blue GAW.[5b]

For cyclic ketones, $k_{DI}$ was found to be strongly ring-size dependent and only cyclohexanone was found to be a considerably better catalyst than acetone (entries 1, 9 and 10). Up to now, only the rate constant $k_{DI}$ for the cyclohexanone-catalysed decomposition of Caro's acid has been determined.[5] The value of $k_{DI} = 6.9 \times 10^4$ dm$^6$ mol$^{-2}$ s$^{-1}$ at $T = 28$ °C reported by Montgomery is in good agreement with the value of $k_{DI} = 7.2 \times 10^4$ dm$^6$ mol$^{-2}$ s$^{-1}$ determined by the IRL-technique. In agreement with the results reported for the relative values of the rate of the caroate decomposition[5] is the ratio $k_{DI}$(cyclohexanone):$k_{DI}$(acetone). Cycloheptanone shows only 1:40 of the catalytic activity compared to cyclohexanone. The ratio $k_{DI}$(cycloheptanone):$k_{DI}$(cyclohexanone) is in line with the relative values of the decomposition of Caro's acid by cycloalkanones under biphasic conditions[6] and is in the trend observed for the cycloalkanone reduction by $NaBH_4$.[27] For cyclopentanone no $^1O_2$ signal was detected even at high concentrations. This is partly due to the Baeyer–Villiger oxidation of the cyclopentanone to the corresponding lactone. Additionally, unfavourable eclipsing interactions at the α-methylenes by rehybridization of the carbonyl carbon from sp$^2$ to sp$^3$ has been noticed by Denmark *et al.*[12]

Finally, the third-order rate constant for the formation of the dioxirane $k_{DI}$ with *N*,*N*-dimethyl-4-oxopiperidinium nitrate ($DMOP^+NO_3^-$) was found to be significantly higher than the rate constant for acetone (entries 1 and 11). We include this ketone in our investigation because it was reported that $DMOP^+NO_3^-$ enhanced dramatically the caroate decomposition in aqueous solutions at pH 9.0[5] and under biphasic conditions at pH 7.8.[12] Most likely this increase is based on an electron-withdrawing effect, leading to an enhanced electrophilicity of the carbon of the carbonyl group and, accordingly, to an enhanced nucleophilic attack by the caroate. However, a considerable difference is observed between the values $k_{DI}(DMOP^+NO_3^-)$:$k_{DI}$(acetone) at pH 10.0 and the corresponding ratio for the rates of the decomposition of Caro's acid determined by Montgomery[5] at pH 9.0. In the following, the effect of pH on the third-order rate constant of the dioxirane formation was studied in order to shed more light on the extremely high catalytic activity of $DMOP^+NO_3^-$. At pH 9.0 we observed an increased $k_{DI}$ for $DMOP^+NO_3^-$ determined at pH 10, although as generally observed, $k_{DI}$ is not a function of pH. At pH 9.0 $DMOP^+NO_3^-$ is by a factor of > 1050 more efficient than acetone in the formation of the corresponding dioxirane. This ratio did not significantly change at pH 8.0. The difference in our measurements at pH 10.0 is due to the hydration equilibrium of $DMOP^+NO_3^-$.[28] The equilibrium constant $K_{hyd}$ is a function of the pH and at high pH values only a minor part exists in the keto form.[29]

Interestingly, the relative values of $k_{DI}$ in Table 1 agree well with those obtained for the relative rates of caroate decomposition. At pH 9.0 the catalytic activity of different ketones was found to vary in the order of approximate relative rates: pentan-3-one (0.25) < butan-2-one (0.5) < acetone (1.0) < cyclohexanone (9.4) < $DMOP^+NO_3^-$ (1400).[5] This trend parallels that obtained for the relative rates for $k_{DI}$ in the ketone-catalysed decomposition of Caro's acid determined by the IRL-technique: pentan-3-one (0.25) < butan-2-one (0.6) < acetone (1.0) < cyclohexanone (9.8) < $DMOP^+NO_3^-$ (1050). Despite the unknown discrepancy for $DMOP^+NO_3^-$ we conclude that the caroate decomposition is predominantly determined by $k_{DI} = K_3K_4k_5$ and the second-order rate constant $k_6$ has no significant influence on caroate decomposition.

### $^1O_2$ Phosphorescence emission at different temperatures

The temperature dependence of $I_p$ in the ketone-catalysed decomposition of Caro's acid is determined by the temperature dependence of $k_{obs}$ given in eqn. (8). Neglecting the temperature dependence of the ketone concentration and of $F$, the temperature dependence of $k_{obs}$ is determined by the product of $K_3$, $K_4$ and $k_5$. Consequent measurements of $k_{obs}$ at different temperatures allow only the estimation of an apparent activation energy $E_{aa}$, where $E_{aa}$ is defined by eqn. (20). Here

$$E_{aa} = \Delta H_3^0 + \Delta H_4^0 + E_a(5) \qquad (20)$$

$\Delta H_i^0$ denotes the enthalpies of the equilibria (3) and (4) (Scheme 1) and $E_a$ (5) is the activation energy of the monomolecular process (5).

The Arrhenius plot in Fig. 7 is given for the acetone-catalysed decomposition of Caro's acid at pH 10.0. $E_{aa}$ is found to be 47.8 kJ mol$^{-1}$. Also, the cyclohexanone-catalysed decomposition of Caro's acid was studied at different temperatures. For this reaction a value of $E_{aa}$ = 36.0 kJ mol$^{-1}$ is obtained. It is obvious that the cyclohexanone-catalysed reaction has a lower activation energy compared to acetone, as expected for the more active catalyst. Besides, the activation energy for the ketone-catalysed reaction for both acetone and cyclohexanone is considerably lower than that of the uncatalysed reaction ($E_a$ = 64.8 kJ mol$^{-1}$, see below).

### $^1O_2$ Phosphorescence of the uncatalysed decomposition of Caro's acid

As mentioned, Evans and Upton[4] have shown that in the uncatalysed decomposition of Caro's acid the evolved oxygen is quantitatively formed as $^1O_2$. The second-order rate constant for this reaction was determined to be $k_2 = 4.7 \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$. The authors have carried out their measurements at pH equal to p$K_{a2}$, whereby the pH was adjusted using NaOH solution. Goodman and Robson[2] have also studied the uncatalysed decomposition of Caro's acid adjusting the pH by using NaOH solutions. These authors determined $k_2$ to be $4.1 \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$.

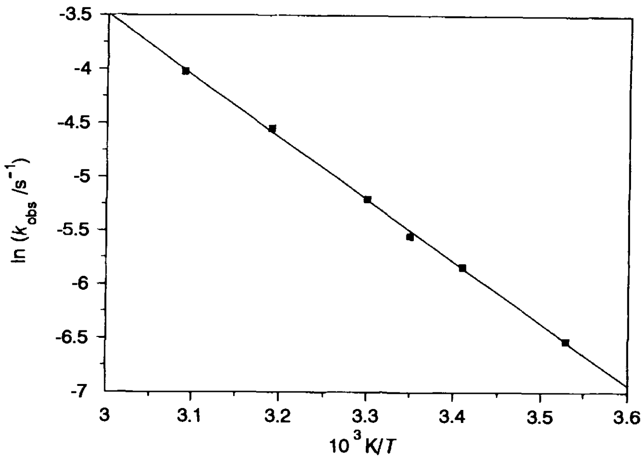

Fig. 7 Plot of ln $k_{obs}$ *versus* $T^{-1}$ for the acetone-catalysed decomposition of Caro's acid. Conditions: $[HSO_5^-]_T(0) = 4.0 \times 10^{-3}$ mol dm$^{-3}$, [acetone] = $3.40 \times 10^{-2}$ mol dm$^{-3}$, [Dequest] = $1.0 \times 10^{-4}$ mol dm$^{-3}$, pH = 10.0.

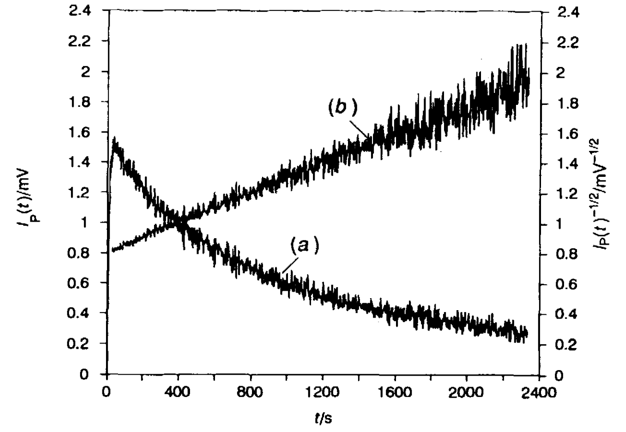

Fig. 8 $I_p(t)$ (*a*) and $1/\sqrt{I_p(t)}$ (*b*) as a function of time for the uncatalysed self-decomposition of Caro's acid. Conditions: $[HSO_5^-]_T(0) = 2.0 \times 10^{-2}$ mol dm$^{-3}$, [Dequest] = $1.0 \times 10^{-4}$ mol dm$^{-3}$, pH = 9.3, $T$ = 25 °C.

We measured the uncatalysed decomposition of Caro's acid at pH 9.3 using carbonate and borate buffer. In agreement with the findings of Goodman and Robson[2] we found that the uncatalysed decomposition of Caro's acid in borate buffer is first-order rather than second-order. The use of borate buffers in the decomposition of Caro's acid should only be made with care. Reproducible results have been obtained in the carbonate buffer. A plot of $I_p(t)$ [curve(*a*)] and $1/\sqrt{I_p(t)}$ [curve(*b*)] at 25 °C as a function of time at pH 9.3 is shown in Fig. 8.

According to eqn. (16) the plot of $1/\sqrt{I_p(t)}$ *versus* time obtained in the carbonate buffer yields a straight line and from the slope of this line $k_2 = 5.9 \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ is obtained. This value is about a factor of 1.3 higher than the values determined by Goodman and Robson[2] and Evans and Upton,[4] respectively. However, our value is about a factor of 3.5 lower than the $k_2$ value determined by Ball and Edwards,[1] who also studied the uncatalysed decomposition of Caro's acid at pH equal to p$K_{a2}$ in carbonate buffer. These authors used high ionic strength of magnitude 1.0–2.3 mol dm$^{-3}$, while Goodman and Robson[2] performed their measurements at an approximately constant ionic strength of 0.2 mol dm$^{-3}$ and in the present work the ionic strength was maintained at about 0.4 mol dm$^{-3}$. The difference in the observed rate constants may be due to the primary kinetic salt effect.

The reaction rate of the uncatalysed decomposition of Caro's acid at pH 9.3 in hydrogencarbonate buffer was also studied over the temperature range of 20–50 °C. The Arrhenius plot results in an activation energy of $E_a = 64.8$ kJ mol$^{-1}$. This activation energy is in agreement with those reported for the uncatalysed decomposition of Caro's acid [1,2] and is higher than the values obtained for the ketone-catalysed decomposition of Caro's acid.

## Conclusions

$^1O_2$ is quantitatively formed both in the uncatalysed self-decomposition of peroxymonosulfuric acid (Caro's acid) and in the ketone-catalysed decomposition of Caro's acid. The rate of $^1O_2$ formation is considerably enhanced in the ketone-catalysed decomposition compared to the self-decomposition of Caro's acid. The formation of $^1O_2$ in a thermal reaction in water can be unequivocally proved by the infrared luminescence (IRL) of $^1O_2$ at 1270 nm, if the rate of $^1O_2$ produced is higher than $2 \times 10^{-7}$ mol dm$^{-3}$ s$^{-1}$. It may be supposed that the decomposition of organic peroxy acids can be catalysed by ketones and that thereby $^1O_2$ is produced as well. We are currently investigating the formation of dioxiranes in the ketone-catalysed decomposition of organic peroxy-acids.

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