New aspects concerning the mechanism of the ketone-catalysed decomposition of Caro's acid

Andreas Lange,[†] **Markus Hild and Hans-Dieter Brauer** *

Institut für Physikalische und Theoretische Chemie, Johann Wolfgang Goethe-Universität Frankfurt a. M., Marie-Curie-Str. 11, D-60439 Frankfurt a. M., Germany

Received (in Cambridge) 12th March 1999, Accepted 27th April 1999

The kinetics of the ketone-catalysed decomposition of peroxymonosulfuric acid (Caro's acid) have been investigated by measuring the phosphorescence of the released singlet molecular oxygen ($^1O_2$) at 1270 nm. As catalysts fluoroacetone, 1,1,1-trifluoroacetone, hexafluoroacetone and *N*,*N*-dimethyl-4-oxopiperidinium nitrate were used. With the exception of fluoroacetone, for the other ketones their third-order rate constant for the formation of the corresponding dioxirane is determined by the pH of the solution. The results are explained on the assumption that for ketones with strong electron-withdrawing groups the keto–*gem*-diol equilibrium and additionally the first dissociation equilibrium of the diol form must be taken into account, if $pH \geq pK_{a1}^{d}$ (where K_{a1}^{d} denotes the first dissociation constant of the diol form). In addition, the apparent activation energy $E_{aa}' = (60 \pm 6)$ kJ mol^{-1} obtained for the *N*,*N*-dimethyl-4-oxopiperidinium nitrate catalysed decomposition of Caro's acid at $pH = 9.0 \ll pK_{a1}^{d}$(*N*,*N*-dimethyl-4-oxopiperidinium-diol) is in agreement with the assumption that a preliminary keto–*gem*-diol equilibrium is involved in the dioxirane formation. Furthermore, the second-order rate constant k_6 for the reaction between dimethyldioxirane and the dianion of Caro's acid (SO_5^{2-}) has been determined by measuring the bleaching of the anionic dye Brilliant Blue G250 by *in situ* generated and by isolated dimethyldioxirane, respectively. This rate constant was found to be $k_6 = (1.6 \pm 0.3) \times 10^3$ dm^3 mol^{-1} s^{-1}. Moreover, the bleaching of Brilliant Blue G250 by other ketone–Caro's acid systems was studied using cyclohexanone, fluoroacetone and *N*,*N*-dimethyl-4-oxopiperidinium nitrate as catalysts. These bleaching experiments yielded the ratio of rate constants k_{13}/k_6, where k_{13} is the second-order rate constant for the reaction between Brilliant Blue G250 and a chosen dioxirane. The values of k_{13}/k_6 vary in a small range between 0.23 (fluoroacetone) and 0.42 (cyclohexanone). k_{13} obtained for the bleaching of Brilliant Blue G250 by dimethyldioxirane amounts to $(5 \pm 1) \times 10^2$ dm^3 mol^{-1} s^{-1}.

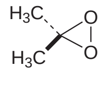
Introduction

It is well known that the decomposition of Caro's acid can be efficiently catalysed by ketones through the formation of intermediate dioxiranes which are powerful and versatile oxygen transfer reagents.[1] Recently we could demonstrate by measuring the infrared phosphorescence of singlet molecular oxygen ($^1O_2$) at 1270 nm that the oxygen evolved in the ketone-catalysed decomposition of Caro's acid is quantitatively produced as $^1O_2$.[2] According to the mechanism postulated by Edwards *et al.*[3] it can be deduced that $^1O_2$ is mainly generated in the reaction between the dioxirane and the dianion (SO_5^{2-}) of Caro's acid.

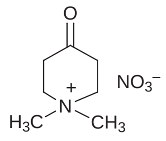
Until now the rate constant of this reaction has been unknown for any dioxirane. This rate constant cannot be determined directly by measuring only the ketone-catalysed decomposition of Caro's acid, because the reaction between the corresponding dioxirane and SO_5^{2-} is faster than the dioxirane formation.

In the current work we want to determine the rate constant for the reaction of dimethyldioxirane (DMD) with SO_5^{2-} dianion. Therefore we have measured the bleaching of the anionic dye Brilliant Blue G250 by isolated dimethyldioxirane and in addition by *in situ* generated dimethyldioxirane. Additionally, we also measured the bleaching of Brilliant Blue G250 by the systems cyclohexanone–, fluoroacetone– and *N*,*N*-dimethyl-4-oxopiperidinium nitrate ($DMOP^+NO_3^-$)–Caro's acid.

Furthermore, in the mechanism developed by Edwards *et al.* for the dioxirane formation in aqueous solution the hydration of ketones was not taken into account. However, especially for ketones with electron-withdrawing groups, *e.g.*, for hexafluoroacetone and for $DMOP^+NO_3^-$ it may be assumed that the keto–*gem*-diol equilibrium substantially influences the rate for the formation of the corresponding dioxirane.[2,4] We also describe the results of a comprehensive study of the effect of ketone hydration on the kinetics using the systems 1,1,1-trifluoroacetone–, hexafluoroacetone– and $DMOP^+NO_3^-$–Caro's acid.



DMD



$DMOP^+NO_3^-$

Experimental

Materials

The anionic dye Brilliant Blue G250 is available from Merck under the trade name Coomassie® and was used as received. The source of potassium peroxomonosulfate (caroate) was the triple salt ($2\ KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) from Fluka and used as such. Dimethyldioxirane (DMD)–acetone solution and Dequest 2066 (Monsanto), an effective metal-chelating agent were kindly denoted by Clariant GmbH, Frankfurt a. M.-Höchst. The solutions of dimethyldioxirane in acetone were prepared as described[5] and assayed for dioxirane content by quantitative oxidation of distilled phenyl methyl sulfide to the

---

[†] *Present address*: J. P. Haas GmbH, Karl-Winnacker-Str. 22, D-36396 Steinau a. d. Str., Germany.

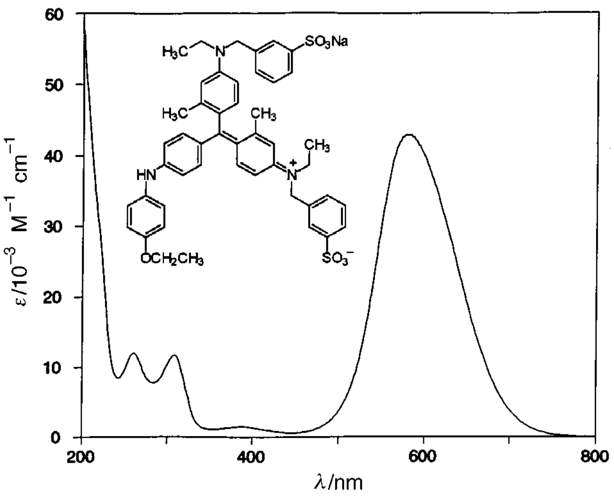


Fig. 1 Absorption spectrum of Brilliant Blue G250 (BB) in water, [BB] = 2.9×10^{-5} mol dm^{-3}, $\varepsilon_{578\ \mathrm{nm}} = 4.3 \times 10^4$ mol^{-1} dm^3 cm^{-1}.

corresponding sulfoxide in acetone-d$_6$ (99.8% from Deutero GmbH) and ^{1}H-NMR spectroscopic determination. The reaction was carried out in alkaline buffer solutions as previously described.[2] The solvent was twice-distilled water. Acetone (Aldrich HPLC grade) and cyclohexanone (Fluka, p.a.) were distilled from dry potassium carbonate prior to use and stored over 4 Å molecular sieves. Fluoroacetone (Aldrich p.a.), 1,1,1-trifluoroacetone (Fluka) and hexafluoroacetone trihydrate (purum, Fluka) were used as received. *N*,*N*-Dimethyl-4-oxopiperidinium nitrate (DMOP$^+$NO$_3^-$) was synthesized by the literature procedure[6] followed by anionic exchange of the requisite iodide salt with silver nitrate.[4]

Apparatus

The pH-measurements were performed using a pH-Meter model WTW pH 525 (Wissenschaftlich-technische Werkstätten). The bleaching of Brilliant Blue G250 was monitored by measuring the absorbance *A* of Brilliant Blue G250 at λ_{max} = 578 nm (see Fig. 1).

In the case of the system ketone–Caro's acid the measurements were performed with a Perkin-Elmer Lambda 5 spectrometer equipped with a temperature control system. The bleaching of Brilliant Blue G250 by isolated dimethyldioxirane was monitored with a RX 1000 stopped flow accessory from Applied Photophysics.[7]

The ^{1}O$_2$ phosphorescence at λ = 1270 nm was recorded with a laboratory made near-infrared luminescence spectrometer.[8,9] For the intensity of the ^{1}O$_2$ phosphorescence emission I_P eqn. (1) holds,[9] where $c = 2.6 \times 10^8$ V dm^3 mol^{-1} s is a constant

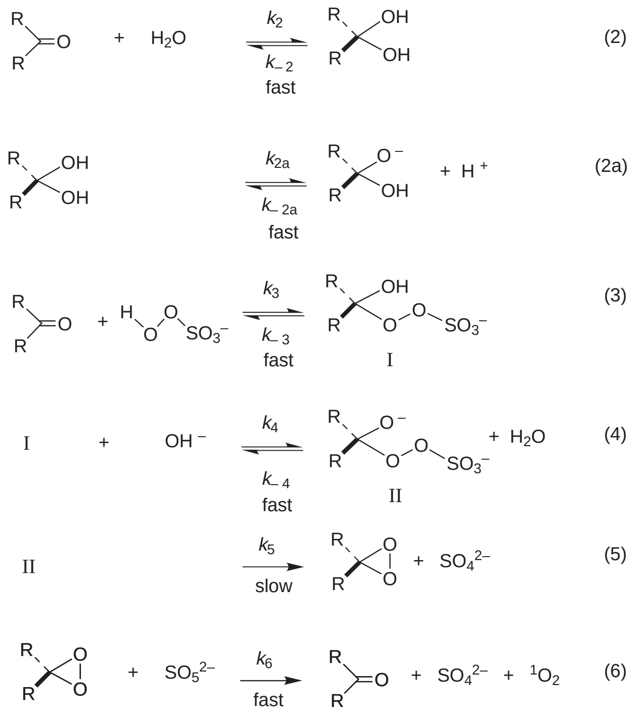
$$I_P = ck_P\tau_\Delta \frac{d[^1O_2]}{dt} \qquad (1)$$

of the infrared luminescence spectrometer, k_P is the rate constant of the ^{1}O$_2$ phosphorescence emission (in water: k_P = 0.18 s^{-1})[10] and τ_Δ the lifetime of ^{1}O$_2$ (in water: τ_Δ = 4.2 μs).[11] d[^{1}O$_2$]/d*t* denotes the rate of ^{1}O$_2$ formation.

Reactions were carried out in thermostatted 1 cm quartz cuvettes. To the buffer–Dequest–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 2.0×10^{-3} to 2.0×10^{-2} mol dm^{-3}.

Expression for I_P of the ketone-catalysed decomposition of Caro's acid

Scheme 1 shows the mechanism of the ketone-catalysed decomposition of Caro's acid taking into account the hydration equilibrium between the ketone and its *gem*-diol [eqn. (2)] and in addition the dissociation equilibrium of the diol form [eqn. (2a)].



Scheme 1

On the basis of Scheme 1, for $I_P(t)$ eqn. (7) can be derived,[2]

$$I_P(t) = I_P(0)\exp(-2k_{obs}t) \qquad (7)$$

where $I_P(0)$, the initial ^{1}O$_2$ phosphorescence intensity, is defined by eqn. (8). $[HSO_5^-]_T(0)$ denotes the total concentration of

$$I_P(0) = ck_P\tau_\Delta k_{obs}[HSO_5^-]_T(0) \qquad (8)$$

caroate at time $t = 0$. For the pseudo first-order rate constant k_{obs} eqn. (9) holds, where K_3 and K_4 are the constants of the

$$k_{obs} = K_3K_4k_5[\text{ketone}]_{eq}F \qquad (9)$$

equilibria (3) and (4) and k_5 is the first-order rate constant of the rate determining step for the formation of the reactive dioxirane from the intermediate II. The factor *F* is a constant at given pH and is defined by eqn. (10). Here K_W is the ionic

$$F = \frac{K_W}{[H^+] + K^c_{a2}} \qquad (10)$$

product of water and $K^c_{a2} = 3.98 \times 10^{-10}$ mol dm^{-3} is the second dissociation constant of Caro's acid. Finally, $[\text{ketone}]_{eq}$ in eqn. (9) represents the equilibrium concentration of the keto form which is connected to the total concentration by eqn. (11), where $[\text{ketone}]_T$ is the total concentration of the ketone, K_H

$$[\text{ketone}]_{eq} = \frac{[\text{ketone}]_T}{1 + K_H(1 + K^d_{a1}/[H^+])} \qquad (11)$$

denotes the constant of equilibrium (2) and K^d_{a1} represents the first acid constant of the diol form according to equilibrium (2a).

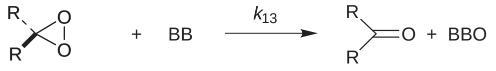
Thus for k_{obs} eqn. (12) follows. When the inequality pH $\ll$ pK^d_{a1} holds, *i.e.* at pH where equilibrium (2a) can be neglected,

$$k_{\text{obs}} = \frac{K_3K_4k_5[\text{ketone}]_\text{T}F}{1 + K_\text{H}(1 + K^\text{d}_{\text{a1}}/[\text{H}^+])} \qquad (12)$$

$[\text{ketone}]_\text{eq}$ becomes independent of pH and as a consequence the denominator in eqn. (11) and (12) is equal to $(1 + K_\text{H})$.

Rate law of the bleaching of Brilliant Blue G250 by the ketone–Caro's acid system

For the bleaching (oxidation) of Brilliant Blue G250 (BB) by ketone–Caro's acid systems Scheme 1 must be expanded by introducing the reaction (13).



(13)

Montgomery[1a,12] was the first to demonstrate that the oxidation power of Caro's acid is enhanced in the presence of ketones. As an example, he tested the oxidation power of ketone–Caro's acid systems by measuring the bleaching of the anionic dye Polar Brilliant Blue GAW (PB). For the rate of bleaching he has found eqn. (14).

$$-\frac{\text{d[PB]}}{\text{d}t} = k_{14}[\text{ketone}][\text{HSO}_5^-][\text{PB}] \qquad (14)$$

If the ketone and Caro's acid are present in amounts such that their concentrations remain essentially constant relative to that of Polar Brilliant Blue GAW being oxidised throughout the reaction, k_{14}, [ketone] and $[\text{HSO}_5]$ can be combined into a single rate constant k_ox, giving a Polar Brilliant Blue GAW rate equation [eqn. (15)], wherein $k_\text{ox} = k_{14}[\text{ketone}][\text{HSO}_5^-]$. It is interesting to note that $-\text{d[PB]}/\text{d}t$ is independent of pH.

$$-\frac{\text{d[PB]}}{\text{d}t} = k_\text{ox}[\text{PB}] \qquad (15)$$

On the basis of the expanded Scheme 1, neglecting equilibrium (2a) for the bleaching of Polar Brilliant Blue GAW and Brilliant Blue G250 (BB), respectively (*vide supra*), eqn. (16) can be derived.

$$-\frac{\text{d[BB]}}{\text{d}t} = \frac{k_{13}[\text{BB}]}{k_{13}[\text{BB}] + k_6[\text{SO}_5^{2-}]} \cdot \frac{K_3K_4k_5[\text{ketone}]_\text{T}[\text{OH}^-][\text{HSO}_5^-]}{1 + K_\text{H}} \qquad (16)$$

With $[\text{HSO}_5^-]_\text{T} = [\text{HSO}_5^-] + [\text{SO}_5^{2-}]$ and $k_6[\text{SO}_5^{2-}] \gg k_{13}[\text{BB}]$ one obtains in accordance with (15) also a pseudo first-order equation [eqn. (17)], where the pseudo first-order rate constant of the bleaching k_bl is defined by eqn. (18).

$$-\frac{\text{d[BB]}}{\text{d}t} = k_\text{bl}[\text{BB}] \qquad (17)$$

$$k_\text{bl} = \frac{k_{13}}{k_6} \cdot \frac{K_3K_4k_5[\text{ketone}]_\text{T}K_\text{W}}{(1 + K_\text{H})K^\text{c}_{\text{a2}}} \qquad (18)$$

In accordance with the findings of Montgomery,[12] the rate of bleaching is independent of pH if equilibrium (2a) is neglected. This is valid as long as the inequality $[\text{SO}_5^{2-}] \gg [\text{BB}]$ remains. Additionally, it is seen that the rate of bleaching becomes zero-order in $[\text{HSO}_5^-]_\text{T}$ according to eqn. (18), whereas Montgomery has postulated but not tested that the rate of bleaching should be first-order with respect to $[\text{HSO}_5^-]_\text{T}$. Nevertheless, the knowledge of k_bl [eqn. (18)] and of k_obs [eqn. (12)] enables us to calculate the ratio k_{13}/k_6 for a given ketone.

Rate law of the bleaching of Brilliant Blue G250 (BB) by isolated dimethyldioxirane

The rate of reaction (13) is kinetically expressed by eqn. (19)

$$-\frac{\text{d[BB]}}{\text{d}t} = k_{13}[\text{DMD}][\text{BB}] \qquad (19)$$

and with high excess of dimethyldioxirane (DMD) relative to Brilliant Blue G250 eqn. (20) holds, where $k_{20} = k_{13}[\text{DMD}]$.

$$-\frac{\text{d[BB]}}{\text{d}t} = k_{20}[\text{BB}] \qquad (20)$$

Results and discussion

Influence of equilibria (2) and (2a) on the dioxirane formation

In the preceding paper[2] the experimental results were interpreted according to the mechanism presented in Scheme 1 neglecting equilibrium (2) and equilibrium (2a). Under these conditions the ketone concentration $[\text{ketone}]_\text{eq}$ has to be assumed identical with the total ketone concentration $[\text{ketone}]_\text{T}$ and from the slope *SL* of the linear correlation of k_obs *versus* $[\text{ketone}]_\text{T}$ according to eqn. (9) the third-order rate constant k_Di for the dioxirane formation is obtained [eqn. (21)]. This rate constant

$$k_\text{Di} = K_3K_4k_5 \qquad (21)$$

can be regarded as a measure of reactivity of a ketone (in the keto form) towards the HSO_5^- anion finally forming the corresponding dioxirane.

However, if equilibrium (2) takes place, $[\text{ketone}]_\text{eq}$ is equal to $[\text{ketone}]_\text{T}/(1 + K_\text{H})$ and from *SL* of the plot k_obs *versus* $[\text{ketone}]_\text{T}$ a third-order rate constant k'_Di is obtained which is defined by eqn. (22).

$$k'_\text{Di} = \frac{k_\text{Di}}{1 + K_\text{H}} \qquad (22)$$

If additionally equilibrium (2a) is involved then eqn. (12) holds true and the slope of k_obs *versus* $[\text{ketone}]_\text{T}$ includes the pH dependent rate constant k''_Di. According to eqn. (23) k''_Di decreases with increasing pH at values of pH > $\text{p}K^\text{d}_\text{a1}$.

$$k''_\text{Di} = \frac{k_\text{Di}}{1 + K_\text{H}(1 + K^\text{d}_{\text{a1}}/[\text{H}^+])} \qquad (23)$$

For most of the ketones investigated previously[2] it can be assumed that the value K_H is much smaller than one and accordingly the rate constant of the dioxirane formation is equal to k_Di. However, for electronically activated ketones carrying an electron-withdrawing group, *e.g.*, for 1,1,1-trifluoroacetone this is not quite right. From the values of k_obs obtained for fluoroacetone and 1,1,1-trifluoroacetone under the same conditions[2] according to eqn. (12) approximately equal values of k''_Di can be estimated: $k''_\text{Di}(\text{fluoroacetone}) = 1.5 \times 10^5\ \text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1} \approx k''_\text{Di}(1,1,1\text{-trifluoroacetone}) = 1.0 \times 10^5\ \text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1}$ at $T = 10$ °C. This result can be a hint that, at least in the case of 1,1,1-trifluoroacetone, equilibrium (2) and probably also equilibrium (2a) plays an important role in the methyl(trifluoromethyl)dioxirane formation (*vide infra*).

It is well known that the diol form of equilibrium (2) [and as a consequence equilibrium (2a)] is favoured by electron-withdrawing substituents bonded to the carbonyl group[13] or by electron-withdrawing groups like the ammonium group[14] as demonstrated by the values of K_H in the following sequence (K_H is given in parentheses): acetone (1.4×10^{-3}, 35 °C)[15] $\ll$ fluoroacetone (1.7×10^{-1}, 25 °C)[16] $\ll$ 1,1,1-trifluoroacetone (35,

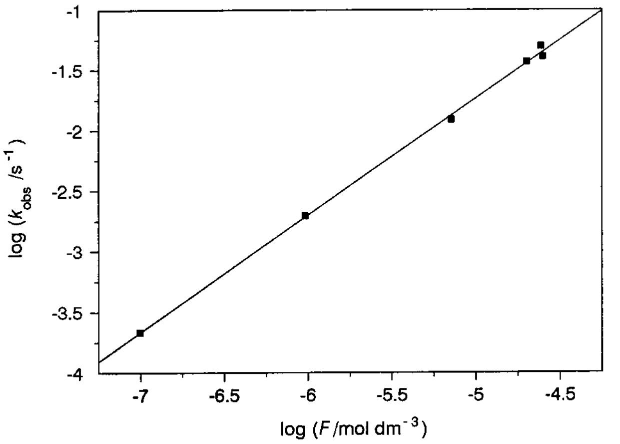


Fig. 2 Double logarithmic plot of log k_{obs} *versus* log F for the fluoroacetone-catalysed decomposition of Caro's acid. Conditions: $[HSO_5^-]_T(0) = 4.0 \times 10^{-3}$ mol dm^{-3}, $[\text{fluoroacetone}]_T = 4.9 \times 10^{-3}$ mol dm^{-3}, [Dequest] = 1.0×10^{-4} mol dm^{-3}, $T = 30$ °C.

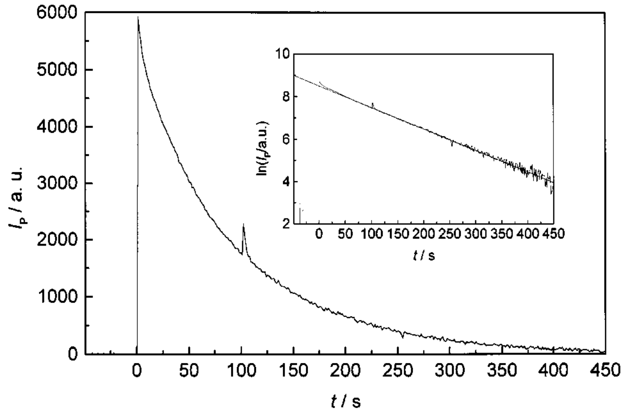


Fig. 3 $I_P(t)$ as a function of time for the hexafluoroacetone-catalysed decomposition of Caro's acid. Conditions: $[HSO_5^-]_T(0) = 1.7 \times 10^{-2}$ mol dm^{-3}, $[\text{hexafluoroacetone}]_T = 2$ mol dm^{-3}, [hexafluoroacetone Na salt]$_T$ = 2 mol dm^{-3}, $T = 25$ °C, pH = 6.7. The inset shows the corresponding plot of ln $I_P(t)$ *versus* time.

35 °C)[17] < $DMOP^+NO_3^-$ (>100, 32 °C)[14] $\ll$ hexafluoroacetone (1.2 × 10^6, 25 °C).[16]

On the basis of the values of K_H observed for acetone it follows that equilibria (2) and (2a) do not influence the dioxirane formation considerably, *i.e.* the rate constant for the formation of the dioxirane is given by k_{Di}. Using fluoroacetone the equilibrium (2a) can also be neglected and consequently the rate constant is equal to k'_{Di}. In accordance with these predictions we found that the double logarithmic plot of k_{obs} *versus* the factor $F = K_W/([H^+]+K^C_{a2})$ yields a straight line for both ketones with a slope equal to 1.00 ± 0.02. This indicates that k_{obs} is directly proportional to the factor F for both acetone and fluoroacetone and that k_{Di} and also k'_{Di} are in fact independent of pH. Fig. 2 shows such a plot obtained for the fluoroacetone-catalysed decomposition of Caro's acid. This relation has been shown recently in our kinetic study using acetone and cyclohexane as catalyst.[2]

In contrast to fluoroacetone equilibrium (2) and additionally equilibrium (2a) must be taken into account for 1,1,1-trifluoroacetone, $DMOP^+NO_3^-$, and especially for hexafluoroacetone. The values of the first acid constants of the diols are: $K^d_{a1}(DMOP^+NO_3^-, \text{diol}) = 6 \times 10^{-11}$ mol dm^{-3} and K^d_{a1}(hexafluoroacetone-diol) = 2×10^{-7} mol dm^{-3}.[18]

Determination of the K^d_{a1} value of 1,1,1-trifluoroacetone by potentiometric titration of the diol form with 1 M NaOH solution resulted in K^d_{a1}(1,1,1-trifluoroacetone-diol) = 2×10^{-11} mol dm^{-3}, whereas from eqn. (23), using the k''_{Di} values given in Table 1, K^d_{a1}(1,1,1-trifluoroacetone-diol) = 6×10^{-11} mol dm^{-3} was estimated. Both results agree well within the error limits. The K^d_{a1} value of the diol of $DMOP^+NO_3^-$ was also estimated according to eqn. (23) using the pH-dependent k''_{Di} values of Table 1. For $DMOP^+NO_3^-$ as catalyst we had already found that the rate constant of the dioxirane formation was pH dependent,[2] but at that time we had no plausible explanation for this unusual result.

On account of the K_H value and the K^d_{a1} value of hexafluoroacetone it may be assumed that the k''_{Di} values of hexafluoroacetone should be smaller compared to those of fluoroacetone and 1,1,1-trifluoroacetone and additionally they should be strongly pH dependent at pH values > 6.0. To determine the catalytic activity of hexafluoroacetone we investigated the hexafluoroacetone-catalysed decomposition of Caro's acid under different conditions.

First of all we measured the rate under the same conditions used for acetone as catalyst. The conditions were: pH = 9.0; $T = 25$ °C; $[\text{hexafluoroacetone}]_T = 7.0 \times 10^{-4}$ mol dm^{-3}, $[HSO_5^-]_T(0) = 5.0 \times 10^{-3}$ mol dm^{-3}, [Dequest] = 1.0×10^{-4} mol dm^{-3}. In contrast to acetone no $^1O_2$ signal was detected for hexafluoroacetone. This result serves to illustrate the very small concentration of the keto form of hexafluoroacetone under these conditions. According to eqn. (11) the value of $[\text{hexafluoroacetone}]_{eq}$ can be estimated as $[\text{hexafluoroacetone}]_{eq} = 3.5 \times 10^{-12}$ mol dm^{-3}.

Secondly, we can state that at pH = 9.0 the rate of dioxirane formation is considerably smaller in the case of hexafluoroacetone than in that of acetone. However, $^1O_2$ generation clearly could be observed under the conditions $[\text{hexafluoroacetone}]_T = 4.0$ mol dm^{-3} at pH = 6.7, *i.e.* at a pH value equal to the pK^d_{a1} value. In Fig. 3 a plot of $I_P(t)$ observed for the hexafluoroacetone-catalysed decomposition of Caro's acid *versus* time is depicted. The corresponding plot of ln $I_P(t)$ *versus* time resulted in a straight line with a slope equal to $-2k_{obs}$ and is shown in the inset of Fig. 3. The straight line 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. (7). The value of the observed rate constant was determined as $k_{obs} = 8.5 \times 10^{-3}$ s^{-1}. With $F = 5.0 \times 10^{-8}$ mol dm^{-3} at pH = 6.7 and $[\text{hexafluoroacetone}]_T = 4.0$ mol dm^{-3} according to eqn. (12), from k_{obs} a value of $k''_{Di} = 4.3 \times 10^4$ dm^6 mol^{-2} s^{-1} was estimated. $^1O_2$ generation could also be detected using the following conditions for the hexafluoroacetone-catalysed decomposition of Caro's acid: pH = 9.0, $[\text{hexafluoroacetone}]_T = 4.0$ mol dm^{-3} and $[HSO_5^-]_T(0) = 5.0 \times 10^{-3}$ mol dm^{-3}. Under these conditions a value of $k''_{Di} = 4.3 \times 10^2$ dm^6 mol^{-2} s^{-1} would be evaluated (see Table 1, entry 5).

The rate constants of the ketone-catalysed decomposition of Caro's acid determined for acetone, fluoroacetone, 1,1,1-trifluoroacetone, $DMOP^+NO_3^-$ and hexafluoroacetone at different pH values are summarized in Table 1.

The values of the ratio k_{Di}(ketone)/k_{Di}(acetone) given in Table 1 demonstrate that hexafluoroacetone in its keto form is the most reactive ketone investigated by us. The keto form reacts with HSO_5^- to the corresponding dioxirane about 2×10^7 times faster than acetone. However, as the values of the ratio of k''_{Di}(ketone)/k''_{Di}(acetone) show, the rate constant of the dioxirane formation and therefore the catalytic activity of hexafluoroacetone is very small compared to that of fluoroacetone, 1,1,1-trifluoroacetone and especially $DMOP^+NO_3^-$ under the same conditions. At pH = 9.0 the rate of the dioxirane formation of hexafluoroacetone is even smaller than that of acetone.

Probably the rate constant k_{Di}(ketone) can also be regarded as a measure of the reactivity of the isolated dioxirane towards olefins. It is reasonable to assume that the isolated methyl(fluoromethyl)dioxirane reacts 52 times faster with a given olefin to give the corresponding epoxide than dimethyldioxirane, or that methyl(trifluoromethyl)dioxirane (MTFD) reacts 1000 times faster than dimethyldioxirane (DMD). In fact, for

Table 1 Rate constants of the ketone-catalysed decomposition of Caro's acid

Entry	Ketone	T/K	pH	k''_{Di}/dm^6 mol^{-2} s^{-1}	$k_{Di} = K_3K_4k_5$/dm^6 mol^{-2} s^{-1}	$\frac{k''_{Di}(\text{ketone})}{k''_{Di}(\text{acetone})}$	$\frac{k_{Di}(\text{ketone})}{k_{Di}(\text{acetone})}$
1	Acetone[a]	298	10.0	5.7×10^{3} [b]	5.7×10^3	1	1
		283	10.0	2.1×10^{3} [b]	2.1×10^3	1	1
2	Fluoroacetone[a]	283	10.0	1.1×10^{5} [b]	1.1×10^5	52	52
3	1,1,1-Trifluoroacetone	283	10.0	1.0×10^{5} [b]	5.7×10^6	48	2.7×10^3
		283	8.0[c]	1.6×10^5	5.8×10^6	76	
4	DMOP$^+$NO$_3^-$	298	10.0	3.5×10^{6} [b]	$\geq 5.6 \times 10^{8}$ [f]	614	1.0×10^5
		298	9.0	6.0×10^{6} [b]	$\geq 6.4 \times 10^{8}$ [f]	1050	
		298	8.0[d]	5.7×10^6	$\geq 5.8 \times 10^{8}$ [f]	1000	
5	Hexafluoroacetone	298	9.0	4.3×10^2	8.6×10^{10}	0.08	1.5×10^7
		298	6.7[e]	4.3×10^4	8.6×10^{10}	7.5	

[a] The rate constants of the dioxirane formation found for acetone and FA are independent of pH, k''_{Di}(acetone) = k_{Di}(acetone), k''_{Di}(FA) = k_{Di}(FA). [b] From ref. 2. [c] Conditions: [TFA] = 2.9×10^{-2} mol dm^{-3}, $[HSO_5^-]_T(0) = 4.0 \times 10^{-3}$ mol dm^{-3}, [Dequest] = 1.0×10^{-4} mol dm^{-3}. [d] Conditions: $[DMOP^+NO_3^-] = 3.6 \times 10^{-4}$ mol dm^{-3}, $[HSO_5^-]_T(0) = 4 \times 10^{-3}$ mol dm^{-3}, [Dequest] = 1.0×10^{-4} mol dm^{-3}. [e] Conditions: see discussion section. [f] Lower limit, calculated using $K_H = 100$.

the ratio of the second-order rate constants k_{ox}(MTFD)/k_{ox}(DMD) in the oxidation of cumene[19] and of silanes,[20] respectively, a value of 600 was found. This value agrees well within the order of magnitude with the one determined for the ratio k_{Di}(1,1,1-trifluoroacetone)/k_{Di}(acetone).

Consequently, there is good reason to suppose that the isolated dioxirane generated by DMOP$^+$NO$_3^-$ or by hexafluoroacetone is much more effective in epoxidation of olefins compared to dimethyldioxirane, but these preformed highly volatile species, so far, are not available.

From the values of the rate constant of dioxirane formation obtained for fluoroacetone and 1,1,1-trifluoroacetone under the aqueous conditions it can be deduced that the epoxidation power in a biphasic system is similar for both ketones although their reactivities towards olefins differ by a factor of about 50. Assuming that a biphasic system must be used for the epoxidation reaction and taking into account that the rate determining step is the formation of the dioxirane, there is no advantage in using 1,1,1-trifluoroacetone instead of fluoroacetone due to the better handling of fluoroacetone by comparison with 1,1,1-trifluoroacetone.

Furthermore it is interesting to note that the graduation found for the k_{Di} values cannot be explained only by the graduation of K_3, the equilibrium constant for the formation of the tetrahedral Criegee intermediate I. Generally it can be assumed that the value of K_H for a given ketone correlates with its value of K_3, *i.e.* a high K_H value implies a high K_3 value, whereby the K_3 value should be higher than that of K_H, since HSO_5^- anion is a better nucleophile compared to water, so that it is considerably more effective than the latter in carrying out the addition step. Besides this, the graduation observed in the K_H values of different ketones should be approximately the same in their K_3 values.

The corresponding K_H values of 1,1,1-trifluoroacetone and DMOP$^+$NO$_3^-$ differ by a factor of about >3, on the other hand the k_{Di} values of both ketones differ by a factor >100. Consequently it may be assumed that the difference in the k_{Di} values is attributed most probably to the difference in the values of the rate constant k_5. Possibly, the separation of the SO_4^{2-} anion from the intermediate II during dioxirane formation occurs considerably faster in the case of DMOP$^+$NO$_3^-$ than in the case of 1,1,1-trifluoroacetone.

Comparing the k_{Di} values of hexafluoroacetone and DMOP$^+$NO$_3^-$, respectively, one can argue in an analogous manner. The K_H value of hexafluoroacetone is 10^4 times higher than that of DMOP$^+$NO$_3^-$. On the other hand, the k_{Di} values differ only by a factor of 100. Again the separation of the SO_4^{2-} anion from the intermediate II of DMOP$^+$NO$_3^-$ seems to occur distinctly faster than that of hexafluoroacetone.

The highest catalytic activity of the ketones investigated is observed for DMOP$^+$NO$_3^-$. The k''_{Di} values depend on pH, but the fact that values of k''_{Di} obtained at pH = 8.0 and pH = 9.0 are equal within the experimental errors indicates that at pH ≤ 9.0 the equilibrium (2a) can be neglected in a first approximation. Therefore the rate constant of the dioxirane formation is given by eqn. (24).

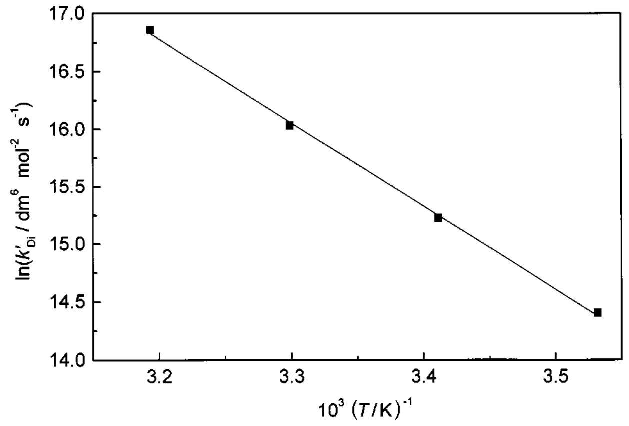


Fig. 4 Plot of ln k'_{Di} *versus* T^{-1} for the DMOP$^+$NO$_3^-$ catalysed decomposition of Caro's acid. Conditions: $[HSO_5^-]_T(0) = 2.7 \times 10^{-3}$ mol dm^{-3}, $[DMOP^+NO_3^-]_T = 4.9 \times 10^{-4}$ mol dm^{-3}, [Dequest] = 1.0×10^{-4} mol dm^{-3}, pH = 9.0.

$$k_{Di}'(\text{DMOP}^+;\ \text{pH} \leq 9.0) \approx \frac{K_3K_4k_5}{1 + K_H} \qquad (24)$$

Since equilibrium (2) with a K_H value ≫ 1 is attributed with a negative value of $\Delta H°$ it can be expected that the apparent activation energy of the dioxirane formation in the case of DMOP$^+$NO$_3^-$ exhibits a relatively high value. To test this assumption we determined the k'_{Di} values at pH = 9.0 as a function of the temperature. In Fig. 4 the Arrhenius plot of the DMOP$^+$NO$_3^-$ catalysed decomposition of Caro's acid is depicted. The apparent Arrhenius parameters A'_a and E'_{aa} estimated from this plot together with the apparent parameters A_a and E_{aa} determined for the system acetone–Caro's acid[2] are given in Table 2. Additionally for comparison the activation energy E_a obtained for the uncatalysed decomposition of Caro's acid[2] is presented in Table 2.

According to eqn. (22) the apparent Arrhenius parameters are defined by eqn. (25) and (26), where $A(5)$ and $E_a(5)$ are the

$$A'_a = A(5)\exp[(\Delta S°_3 + \Delta S°_4 - \Delta S°_H)/R] \qquad (25)$$

$$E'_{aa} = \Delta H°_3 + \Delta H°_4 + E_a(5) - \Delta H°_H \qquad (26)$$

Arrhenius parameters of the monomolecular process (5) and $\Delta S°_i$ and $\Delta H°_i$ denote the entropies and enthalpies, respectively, of the equilibria (2), (3) and (4).

As the values presented in Table 2 demonstrate, the value of E'_{aa} is higher than the value of E_{aa} determined for the acetone catalysis. Furthermore, E'_{aa} resembles the activation energy E_a of the uncatalysed decomposition of Caro's acid. Obviously, both results indicate that equilibrium (2) significantly influences the formation of the corresponding dioxirane in the $DMOP^+NO_3$-catalysed decomposition of Caro's acid at pH = 9.0.

For a more detailed discussion the thermodynamic data ($\Delta S°_H$ and $\Delta H°_H$) of the hydration equilibrium (2) of $DMOP^+$-NO_3^- are required. Although experimental data are unknown, values of $\Delta S°_H$ and $\Delta H°_H$ can be estimated approximately. As shown by Buschmann *et al.*,[16] addition of water to ketones is sensitive to electronic effects but not to steric effects.[16] As an example, for amino-4-oxopiperidinium hydrochloride and for many other ketones a value of $\Delta S°_H = -80$ e.u. was determined.[14] Considering this value and an approximate value of $K_H = 100$ for the equilibrium (2) of $DMOP^+NO_3^-$ a value of $\Delta H°_H = -36$ kJ mol^{-1} can be estimated, *i.e.* $\Delta H°_H$ contributes to E'_{aa} considerably. Taking as a basis the values of $\Delta S°_H = -80$ e.u. and $\Delta H°_H = -36$ kJ mol^{-1} for an estimation of the apparent Arrhenius parameter A_a and E_{aa} responsible for the temperature dependence of the rate constant k_{Di} the following values are obtained: $A_a = A'_a \exp(\Delta S°_H/R) = 3 \times 10^{13}$ dm^6 mol^{-2} s^{-1} and $E_{aa} = E'_{aa} + \Delta H°_H = 26$ kJ mol^{-1}.

The comparison of these values with those found for the acetone-catalysed decomposition of Caro's acid demonstrates that $A_a(DMOP^+NO_3^-)$ is ten times higher than A_a(acetone) and $E_{aa}(DMOP^+NO_3^-)$ is clearly lower than E_{aa}(acetone). Both results are in agreement and confirm the fact that the keto form of $DMOP^+NO_3^-$ is much more effective in dioxirane formation compared to the keto form of acetone.

Bleaching of Brilliant Blue G250 by ketone–Caro's acid systems

From eqn. (17) it can be deduced that a plot of the absorbance A of Brilliant Blue G250 *versus* time should result in a monoexponential decay. Fig. 5 shows such a plot for the system acetone–Caro's acid. The corresponding plot of $\ln(A/A_0)$ *versus* time is depicted in the inset of Fig. 5. This plot yields an approximately straight line till 6000 s with a slope equal to $-k_{bl} = -(3.1 \pm 0.7) \times 10^{-4}$ s^{-1} and is linear through about three half-lives. Similar plots were observed at pH = 9.0 for the other ketone–Caro's acid systems, too. The values of k_{bl} given in Table 3 are mean values of at least five experimentally determined k_{bl} values. Additionally, in Table 3 the concentration of the ketones and the rate constants k_{Di} and k'_{Di}, respectively, used for the calculation of the ratio k_{13}/k_6 are presented. Furthermore, the values of the rate constant k'_{bl} valid for an actual or extrapolated ketone concentration of 6.7×10^{-3} mol dm^{-3} are also given in Table 3.

Table 2 The apparent Arrhenius parameters for the acetone[2] and the $DMOP^+NO_3^-$ catalysed decomposition of Caro's acid and the activation energy of the uncatalysed decomposition of Caro's acid[2]

Ketone	pH	A_a, A'_a [a]/ dm^6 mol^{-2} s^{-1}	E_{aa}, E'_{aa}, E_a/ kJ mol^{-1}
Acetone[b]	10.0	1×10^{12} [c]	48 ± 3
$DMOP^+NO_3^-$	9.0	2×10^{17} [c]	60 ± 6
HSO_5^-/SO_5^{2-}	9.4	—	65 ± 5

[a] A_a and E_{aa} hold for the temperature dependence of k_{Di}, A'_a and E'_{aa} hold for the temperature dependence of k'_{Di}. [b] At pH = 10, whereby measurements at different values of pH have shown the independence of A_a and E_{aa} of pH. [c] The error in A_a and A'_a amounts to about one order of magnitude.

It is evident from the values of k'_{bl} that the bleaching rate of Brilliant Blue G250 by the ketone–Caro's acid systems strongly depends on ketone structure. The values of k'_{bl} determined for acetone and $DMOP^+NO_3^-$, respectively, differ by a factor of 1000. In contrast, the ratio of the rate constants k_{13}/k_6 is practically independent of the ketone. For the ketones investigated k_{13}/k_6 is found to be lower than one indicating that the *in situ* generated dioxiranes react faster with the SO_5^{2-} anion than with Brilliant Blue G250. Consequently, the dioxiranes are mainly consumed by reaction (6), especially if the concentration of SO_5^{2-} is significantly higher than the Brilliant Blue G250 concentration.‡

Already Edwards *et al.*[3] have pointed out that the yield of epoxidation of olefins by the acetone–Caro's acid system decreases at increasing pH values which is obviously put down to the fact that the more nucleophilic peracid dianion SO_5^{2-} dominates at increasing pH. It should be noted here that for electronically activated ketones like fluoroacetone,

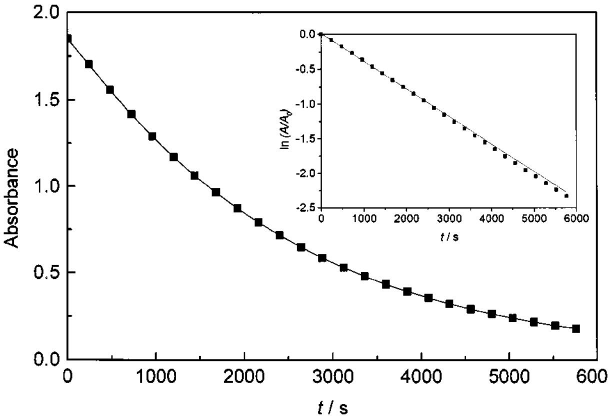


Fig. 5 Absorbance of Brilliant Blue G250 (BB) as a function of time during bleaching with the Caro's acid–acetone system. Conditions: $[HSO_5^-]_T(0) = 3 \times 10^{-3}$ mol dm^{-3}, [acetone] = 6.7×10^{-3} mol dm^{-3}, [BB] = 4.3×10^{-5} mol dm^{-3}, [Dequest] = 1.0×10^{-4} mol dm^{-3}, pH = 9.0, $T = 25$ °C, $\lambda_A = 578$ nm. The inset shows the corresponding plot of $\ln(A/A_0)$ *versus* time.

Table 3 Kinetic data for the bleaching of Brilliant Blue G250 by ketone–Caro's acid systems[a]

Ketone	[Ketone]/ mol dm^{-3}	k_{Di} or k'_{Di} [b]/ dm^6 mol^{-2} s^{-1}	k_{bl} [e]/s^{-1}	k_{13}/k_6	k'_{bl} [f]/s^{-1}	$\frac{k'_{b1}(\text{ketone})}{k'_{b1}(\text{acetone})}$
Acetone	6.7×10^{-3}	5.7×10^{3} [c]	3.1×10^{-4}	0.32	3.1×10^{-4}	1
Cyclohexanone	6.7×10^{-4}	5.6×10^{4} [c]	3.4×10^{-4}	0.42	3.4×10^{-3}	11
Fluoroacetone	2.7×10^{-4}	3.0×10^{5} [c]	4.7×10^{-4}	0.23	1.2×10^{-2}	39
$DMOP^+NO_3^-$	8.0×10^{-6}	6.0×10^{6} [d]	3.0×10^{-4}	0.25	2.5×10^{-1}	807

[a] $[HSO_5^-]_T(0) = 3.0 \times 10^{-3}$ mol dm^{-3}, [BB] = 4.3×10^{-5} mol dm^{-3}, [Dequest] = 1.0×10^{-4} mol dm^{-3}, $NaHCO_3$/NaOH-buffer at pH = 9.0, $T = 25$ °C. [b] Values presented in the preceding work.[2] [c] k_{Di}. [d] k'_{Di}. [e] The error in k_{bl} amounts to about 20%. [f] $k'_{bl} = k_{b1}$ [acetone]/[ketone].

---

‡ In reaction (6) molecular $^1O_2$ is produced. Tests with photochemically generated $^1O_2$ have unequivocally shown that $^1O_2$ cannot bleach Brilliant Blue G250.

1,1,1-trifluoroacetone, and $\mathrm{DMOP^+NO_3^-}$ the same argument holds for a pH range between ≈7.0 and 9.0 (*vide supra*). However, using hexafluoroacetone as catalyst the yield of epoxidation should decrease with increasing pH by both the increase of the $\mathrm{SO_5^{2-}}$ concentration and the distinct decrease of k''_{Di}.

The observation that the values of k_{13}/k_6 of the ketones investigated are very similar is consistent with the result that the values of k'_{bl}(ketone) and k'_{Di}(ketone), respectively, exhibit the same graduation going from acetone *via* cyclohexanone and fluoroacetone to $\mathrm{DMOP^+NO_3^-}$. From this parallelism it can be deduced that the rate of bleaching of Brilliant Blue G250 by the ketone–Caro's acid system is determined by the rate of the dioxirane formation. Consequently, although the methyl(trifluoromethyl)dioxirane is obviously a stronger oxidant than methyl(fluoromethyl)dioxirane[19] it is pointless to use the 1,1,1-trifluoroacetone–Caro's acid systems instead of the fluoroacetone–Caro's acid system at pH < 9.0, since both ketones have approximately the same rate of dioxirane formation.

It should be noted here that the hexafluoroacetone–Caro's acid system can be eliminated as an oxidant system although the bis(trifluoromethyl)dioxirane can be regarded as the most reactive dioxirane, because of the relatively slow rate for the formation of the corresponding dioxiranes already at pH = 7.0 (*vide supra*).

Finally, the graduation observed for the values of k'_{bl} is in excellent agreement with the values of k'_{bl} obtained by Montgomery[12] for the bleaching of Polar Brilliant Blue GAW (PB) using the same ketone–Caro's acid systems. However, the k_{ox} values determined for the bleaching of Polar Brilliant Blue GAW are 10 times higher than the values of k'_{bl} given in Table 3 for Brilliant Blue G250.[21] That can be put down to the fact that Montgomery used an anthraquinone dye and we employed a triphenylmethane dye. It is undoubtedly true that the rate of oxidation taking place will naturally be dependent on the chemical structure of the substrate.

Bleaching of Brilliant Blue G250 by isolated dimethyldioxirane

In order to determine the rate constant k_{13} for the bleaching of Brilliant Blue G250 by dimethyldioxirane we performed experiments with isolated dimethyldioxirane under pseudo first-order conditions using an excess of dimethyldioxirane. The concentrations of dimethyldioxirane used were determined using phenyl methyl sulfide (thioanisole) as described above. It should be pointed out that the aqueous weak alkaline solution chosen for this study was first screened for any conflicting first-order process, *e.g.*, autodecomposition of dimethyldioxirane or second-order processes, *e.g.*, reaction of dimethyldioxirane with the alkaline solution. No interference from these processes was observed. Finally, the kinetics were followed by observing the decay in the absorption band of Brilliant Blue G250 at 578 nm. Fig. 6 shows such a plot of absorbance A of Brilliant Blue G250 *versus* time bleached by isolated dimethyldioxirane (DMD) at pH = 9.0. The plot of $\ln(A/A_0)$ *versus* time gave a straight line with a slope $SL = k_{13}[\mathrm{DMD}]$. The coefficient k_{13} obtained from seven independent determinations was found to be $k_{13} = (5 \pm 1) \times 10^2\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$.

Earlier results reported second-order rate coefficients for some alkene epoxidations by dimethyldioxirane. These studies exhibited k_{epox} values for dimethyldioxirane of *ca.* 10^{-3} to $10^1\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$.[20] In all cases the reported rate constants are lower than those measured here for Brilliant Blue G250. However, there are several reports in which some effect of solvent on reactions of dimethyldioxirane has been found.[22] One of the most comprehensive works to date is that of Baumstark and Vasquez[23] who found that increasing the mole fraction of water in an acetone–water mixture led to an increased rate in the epoxidation of *p*-methoxystyrene by dimethyldioxirane. The lowest rate constant measured by these authors was $0.55\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ for $X(\mathrm{H_2O}) = 0$, which is an order of magnitude lower compared to $6.0\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ at $X(\mathrm{H_2O}) = 0.55$. This rate increase was ascribed to the hydrogen bond donor capacity of the water molecule for the epoxidation reaction[22a] of dimethyldioxirane. In our measurements $X(\mathrm{H_2O})$ amounts to 0.97 so that the origin of the extraordinary increased oxidation rate becomes comprehensible.

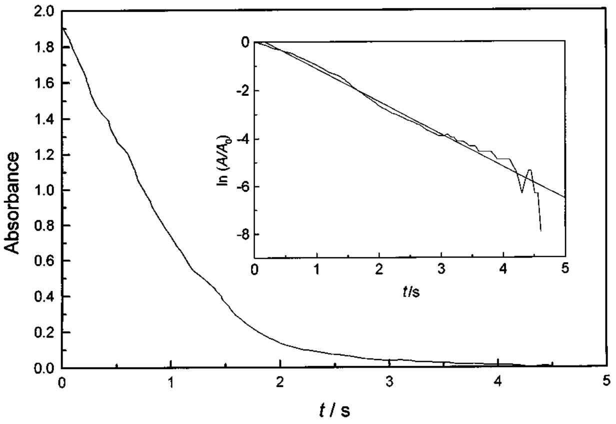


Fig. 6 Absorbance of Brilliant Blue G250 (BB) as a function of time during bleaching with isolated dimethyldioxirane (DMD). Conditions: $[\mathrm{DMD}](0) = 3.0 \times 10^{-3}\ \mathrm{mol\ dm^{-3}}$, $[\mathrm{BB}] = 6.0 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$, pH = 9.0, $T = 25\ ^\circ\mathrm{C}$, $\lambda_{\mathrm{A}} = 578$ nm. The inset shows the corresponding plot of $\ln(A/A_0)$ *versus* time.

The rate constant k_{13} and the ratio k_{13}/k_6 obtained enabled us to calculate the second-order rate constant k_6 in the reaction of dimethyldioxirane and $\mathrm{SO_5^{2-}}$. The reaction was found to have $k_6 = (1.6 \pm 0.3) \times 10^3\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$.

It should be noted that this rate constant (refer to Scheme 1) is significantly larger ($1.6 \times 10^3\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ *versus* $5.9 \times 10^{-2}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$) than that obtained for the uncatalysed self-decomposition of Caro's acid [eqn. (27)]. The higher reactivity

$$\mathrm{HSO_5^- + SO_5^{2-} \xrightarrow{k_{27}} HSO_4^- + SO_4^{2-} + {}^1O_2} \qquad (27)$$

of $\mathrm{SO_5^{2-}}$ toward dimethyldioxirane compared to $\mathrm{HSO_5^-}$ is consistent with the electrophilic nature of dimethyldioxirane, so that it was justified in this study to neglect the uncatalysed decomposition of Caro's acid.

Conclusions

1. Since for a strongly electronically activated ketone the hydration equilibrium (2) must be taken into account, the equilibrium concentration of the keto form, which is necessary for the formation of the corresponding dioxirane, is smaller than the total concentration of the ketone. If in addition to equilibrium (2) the first dissociation equilibrium (2a) of the diol is of importance, the concentration of the keto form of the ketone could become so small that the rate of the formation of the corresponding dioxirane will be very small, although the reactivity of the keto form towards Caro's acid ($\mathrm{HSO_5^-}$ anion) is relatively high.

2. For ketones for which the equilibrium (2) and (2a) must be taken into account one has to distinguish between the reactivity of the ketone towards Caro's acid and its catalytic activity with respect to the decomposition of Caro's acid. A measure for the reactivity of a ketone towards Caro's acid is the rate constant k_{Di} of the dioxirane formation including the formation constant K_3 for the Criegee intermediate I. A measure for the catalytic activity of a ketone with respect to the decomposition of Caro's acid or to another peroxy acid is the rate constant k''_{Di}, which involves besides the value of k_{Di} both equilibrium constants K_{H} and $K^{\mathrm{d}}_{\mathrm{a1}}$.

Acknowledgements

Financial support by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm "Sauerstofftransfer/Peroxidchemie") is gratefully acknowledged. Furthermore we thank Clariant GmbH (Frankfurt a. M.-Höchst, Germany) for a gift of Dequest 2066 and especially Dr Bernd Nestler (Clariant GmbH) for the preparation of the dimethyldioxirane–acetone solution.

References

1 (*a*) R. E. Montgomery, *J. Am. Chem. Soc.*, 1974, **96**, 7820; (*b*) W. Adam, R. Curci and J. O. Edwards, *Acc. Chem. Res.*, 1989, **22**, 205, (*c*) R. W. Murray, *Chem. Rev.*, 1989, **89**, 1187; (*d*) R. Curci, in *Advances in Oxygenated Processes*, ed. A. L. Baumstark, JAI Press, Greenwich, CT, 1990, vol. 2, ch. 1; (*e*) W. Adam, L. P. Hadjiarapoglou, R. Curci and R. Mello, in *Organic Peroxides*, ed. W. Ando, John Wiley and Sons, New York, 1992, ch. 4.

2 A. Lange and H.-D. Brauer, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 805.

3 (*a*) J. O. Edwards, R. H. Pater, R. Curci and F. Di Furia, *Photochem. Photobiol.*, 1979, **30**, 63; (*b*) A. R. Gallopo and J. O. Edwards, *J. Org Chem.*, 1981, **46**, 1684.

4 S. E. Denmark, D. C. Forbes, D. S. Hays, J. S. DePue and R. G. Wilde, *J. Org Chem.*, 1995, **60**, 1391.

5 W. Adam, Y. Y. Chan, D. Cremer, J. Gauss, D. Scheutzow and M. Schindler, *J. Org. Chem.*, 1987, **52**, 2800.

6 H. M. E. Cardwell and F. J. McQuillin, *J. Chem. Soc.*, 1949, 708.

7 H. Jockel and R. Schmidt, *J. Chem. Soc.*, *Perkin Trans. 2*, 1997, 2719.

8 R. Schmidt and H.-D. Brauer, *J. Am. Chem. Soc.*, 1987, **109**, 6976.

9 K. Böhme and H.-D. Brauer, *Inorg. Chem.*, 1992, **31**, 3468.

10 R. Schmidt and E. Afshari, *J. Phys. Chem.*, 1990, **94**, 4377.

11 R. Schmidt, *J. Am. Chem. Soc.*, 1989, **111**, 6983.

12 R. E. Montgomery, U.S. Patent 3,822,144, 1974.

13 R. P. Bell, in *Advances in Physical Organic Chemistry*, ed. V. Gold, Academic Press, New York, 1966, vol. 4, p. 1.

14 J. J. van Luppen, J. A. Lepoivre, R. A. Dommisse and F. C. Alderweireldt, *Org. Magn. Reson.*, 1979, **12**, 399.

15 J. Hine and R. W. Redding, *J. Org. Chem.*, 1970, **35**, 2769.

16 H.-J. Buschmann, H.-H. Füldner and W. Knoche, *Ber. Bunsenges. Phys. Chem.*, 1980, **84**, 41.

17 J. P. Guthrie, *Can. J. Chem.*, 1975, **53**, 898.

18 J. Hine and N. W. Flachskam, *J. Org. Chem.*, 1977, **42**, 1979.

19 (*a*) R. Mello, M. Fiorentino, O. Sciacovelli and R. Curci, *J. Org. Chem.*, 1988, **53**, 3890; (*b*) W. Adam, R. Mello and R. Curci, *Angew. Chem.*, 1990, **102**, 916.

20 (*a*) A. L. Baumstark and C. J. McCloskey, *Tetrahedron Lett.*, 1987, **28**, 3311; (*b*) R. W. Murray and D. L. Shiang, *J. Chem. Soc.*, *Perkin Trans. 2*, 1990, 349; (*c*) R. Curci, A. Dinoi and M. F. Rubino, *Pure Appl. Chem.*, 1995, **67**, 811.

21 We could not test the values of Montgomery since PB is not commercially available.

22 (*a*) R. W. Murray and D. Gu, *J. Chem. Soc.*, *Perkin Trans. 2*, 1993, 2203; (*b*); R. W. Murray and D. Gu, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 451.

23 A. L. Baumstark and P. C. Vasquez, *J. Org. Chem.*, 1988, **53**, 3437.

Paper 9/01976F