Monatshefte für Chemie 133, 1363–1372 (2002)
DOI 10.1007/s00706-002-0488-5

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Kinetics of the Formation of the Blue Complex $CrO(O_2)_2$ Formed by Dichromate and H_2O_2 in Acid Solutions. A Stopped-Flow Investigation Using Rapid-Scan UV-VIS Detection

Günter Grampp*, **Stephan Landgraf**, **Tomasz Wesierski**[a],
Beata Jankowska[a], **Ewa Kalisz**[a], **Dana-Maria Sabou**[b],
and **Boryana Mladenova**[c]

Graz University of Technology, Institute of Physical and Theoretical Chemistry,
A-8010 Graz, Austria

Received January 30, 2002; accepted (revised) June 5, 2002

Summary. The kinetics of the $CrO(O_2)_2$ formation by H_2O_2 and $Cr_2O_7{}^{2-}$ in aqueous acidic media was measured at $293 \pm 2\,K$ in a *pH* range between 2.5 and 3.3. Using the stopped-flow method with rapid scan UV-VIS detection, the rate law of the formation of $CrO(O_2)_2$ was determined. For the media $HClO_4$, HNO_3 and CH_3COOH, the reaction order in the $Cr_2O_7{}^{2-}$ concentration was found to be 0.5. For $[H_2O_2]$ as well as for $[H^+]$, the reaction was first order in all acids used. In HCl and H_2SO_4 media the reaction was first order in $Cr_2O_7{}^{2-}$. At $T = 293 \pm 2\,K$ the rate constant for the formation of $Cr(O)(O_2)_2$ was found to be $(7.3 \pm 1.9) \cdot 10^2\,M^{-3/2}\,s^{-1}$ in $HClO_4$.

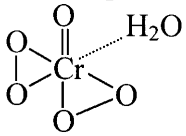
Keywords. Chemical kinetics; Stopped-flow technique; $Cr(O)(O_2)_2$ complex; Reaction order.

Introduction

In strong acidic media the blue $CrO(O_2)_2$ complex (**I**) is formed by the reaction between $Cr_2O_7{}^{2-}$ and H_2O_2. Stabilized by organic solvents like ether, alcohols or pyridine, this complex became an analytical tool for the identification of chromium

---

* Corresponding author. E-mail: grampp@ptc.tu-graz.ac.at
On leave of:
[a] A. Mickiewicz University, Faculty of Chemistry, Dept. of Physical Chemistry, Poznan, Poland
[b] "Babes-Bolyai" University Cluj-Napoca, Faculty of Chemistry, Dept. of Physical Chemistry, Cluj, Romania
[c] Bulgarian Academy of Science, Institute of Catalysis, EPR-Laboratory, Sofia, Bulgaria

(VI) ions. The formation of the blue chromium peroxide complex $CrO(O_2)_2$ has been known and used as an analytical tool [1] for a long time [2]. In neutral or very weakly acidic solutions explosive violet perchromate $[CrO(O_2)_2OH]^-$ is formed [3]. $CrO(O_2)_2$ can be extracted from aqueous solution with ether or amyl acohol. The complex is stabilized by ether, pyridine etc. [4] by reaching the coordination number of six. A pentagonal pyramidal structure is found by X-ray structural analysis [4]. Because of the operational simplicity chromium peroxide is widely used for the oxidation of different alcohols and hydroquinones [5–7]. The $CrO(O_2)_2$ complex has some interesting properties like its solubility in organic solvents, and its relative stability. Recently the specific oxidations of aliphatic alcohols by 2,2′-bipyridyl chromium peroxide and their kinetics have been reported [8]. Chromium peroxide (**I**)  is formed by the reaction [4]:

$$Cr_2O_7{}^{2-} + 4H_2O_2 + 2H^+ \xrightarrow{k} 2\,CrO(O_2)_2 \cdot H_2O + 4H_2O \qquad (1)$$

(*For the sake of brevity* (**I**) *is abbreviated to* $CrO(O_2)_2$ *or even be* CrO_5 *in the following discussion*)

In aqueous solution $CrO(O_2)_2$ stabilizes to $CrO(O_2)_2 \cdot H_2O$. In principle the speciation of Cr(VI) is given by the well-known chromate–dichromate equilibrium (2), together with the protonation equilibria (3) and (4):

$$2HCrO_4{}^- \overset{K_2}{\rightleftharpoons} Cr_2O_7{}^{2-} + H_2O \qquad (2)$$

$$HCrO_4{}^- \overset{K_3}{\rightleftharpoons} CrO_4{}^{2-} + H^+ \qquad (3)$$

$$H_2CrO_4 \overset{K_4}{\rightleftharpoons} HCrO_4{}^- + H^+ \qquad (4)$$

Of these three reactions the dimerization of $HCrO_4{}^-$, Eq. (2), is important within the *pH* range of $2.5 \leq pH \leq 3.3$. The protonations and the dimerization reaction, Eqs. (2–4) are well described by *Haight et al.* [9] and *Tong* [10]. Values reported for the equilibrium according to Eq. (2) are $K_2 = 98\,M^{-1}$ [9] and $K_2 = 158\,M^{-1}$ [11]. The value $K_2 = 44\,M^{-1}$ reported by *Neuss* and *Riemann* [12] and *Howard et al.* [13] deviates considerably. For the deprotonation reaction, Eq. (3), $pK_3 = 5.9$ and $pK_3 = 6.5$ have been found [11, 14]. The first protonation equilibrium of H_2CrO_4, described by Eq. (4), is established only in very acidic solutions and is difficult to measure. pK_4 is reported in the literature as $pK_4 = -0.7$ [9], $pK_4 = -0.26$ [11], and $pK_4 = -0.74$ [15]. Even in concentrated perchloric acid a complete conversion into H_2CrO_4 is not possible [9].

Reviews on dichromate oxidation have been given by *Westheimer* [16] and *Waters* [17]. The UV-VIS spectrum in perchloric media at $2 \leq pH \leq 4$ is due solely to $HCrO_4{}^-$. The same behaviour is found in acetic and nitric media. Hydrochloric and sulfuric acid show a different behaviour. With aqueous HCl, $HCrO_4{}^-$ converts into CrO_3Cl^-, according to:

$$HCrO_4{}^- + H^+ + Cl^- \overset{K_5}{\rightleftharpoons} CrO_3Cl^- + H_2O \qquad (5)$$

Whereas with sulfuric acid, $HCrO_4^-$ reacts as follows:

$$HCrO_4^- + HSO_4^- \overset{K_6}{\rightleftharpoons} CrO_3(OSO_3)^{2-} + H_2O \qquad (6)$$

Reactions (5) and (6) are essentially completed when either 1.0 M HCl or 1.0 M hydrogensulfate [9] is used. There is no change in the chromium redox state.

The blue $CrO(O_2)_2$ complex formed by Eq. (1) decomposes slowly [18, 20] according to Eq. (7).

$$4\,CrO(O_2)_2 + 12\,H^+ \xrightarrow{K_7} 4Cr^{3+} + 6H_2O + 7O_2 \qquad (7)$$

This redox reaction leads to a change in colour, from blue $CrO(O_2)_2$ to violet aqueous Cr_{aq}^{3+} ions.

The aim of this kinetic investigations is to measure the rate constants and the reaction orders of the reactants and the *pH* dependence of the $Cr(O)(O_2)_2$ formation according to Eq. (1) in acidic aqueous solutions.

Results and Discussion

In the UV-VIS spectrum of the $Cr_2O_7^{2-}$ ion in perchloric acid at $pH = 2.5$, peaks at 260 nm and 350 nm are found. The 350 nm absorption can be used to follow the decrease of $Cr_2O_7^{2-}$.

Figure 1 depicts the UV-VIS spectra of $5 \cdot 10\,M^{-4}$ $Cr_2O_7^{2-}$ solution, together with that of CrO_5 stabilized by Et_2O. The absorbance of a $5 \cdot 10^{-4}$ M $Cr_2O_7^{2-}$ solution is E_{350} $(Cr_2O_7^{2-}) = 1.6$ in perchloric acid at $pH = 2.5$. The CrO_5-concentration is obtained as $2.6 \cdot M^{-3}$, from the measured absorbance E_{580} and the extinction coefficient reported as $\varepsilon_{580} = 500\,M^{-1}\,cm^{-1}$ [4]. For $CrO(O_2)_2$ the maximum peak appears at 580 nm where the dichromate shows no absorption. The spectra of $HCrO_4^-$ and $Cr_2O_7^{2-}$ are reported to be very similar [10]. Figure 2 shows rapid-scan spectra in the 320–720 nm range. At various delay times, t_d, after mixing the reactants, each individual UV-VIS spectrum is recorded within 10 ms.

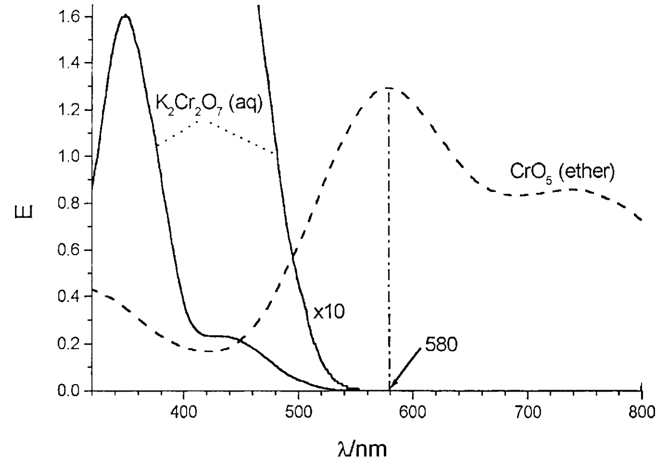


Fig. 1. UV-VIS spectrum of $5 \cdot 10^{-4}$M $Cr_2O_7^{2-}$ in perchloric acid, $pH = 2.5$. The spectrum of $CrO(O_2)_2$ was obtained from $2 \cdot 10^{-2}$M H_2O_2 and $2.5 \cdot 10^{-3}$M $K_2Cr_2O_7$, extracted in 5 ml ether

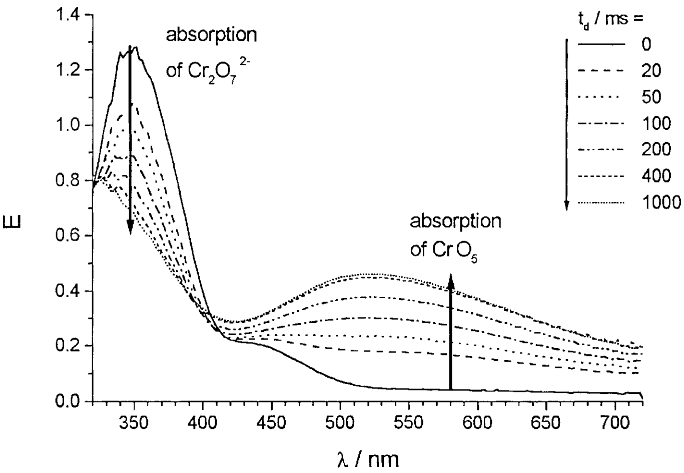


Fig. 2. Rapid scan UV-VIS spectra on the formation of $CrO(O_2)_2$, observed at 580 nm. Each single spectrum is recorded in 10 ms. Concentrations are $[Cr_2O_7^{2-}]_0 = 2.5 \cdot 10^{-3}$ M and $[H_2O_2]_0 = 0.32$ M, $pH = 2.5$ in perchloric acid

A fast increase of $CrO(O_2)_2$ at 580 nm accompanied by a decrease of $Cr_2O_7^{2-}$ at 350 is observed, both saturate after 1000 ms.

Determination of the reaction orders

To obtain the reaction orders involved, the method of the initial rates in connection with the isolation method is used. The initial rate of reaction (1) is described by the following rate law:

$$\left(\frac{d[CrO_5]}{dt}\right) = k[H_2O_2]^a[H^+]^b[Cr_2O_7^{2-}]^c \tag{8}$$

Using *Lambert-Beer*'s law, $E_\lambda = c \cdot l \cdot \varepsilon_\lambda$, one obtains:

$$\log\left(\frac{dE_\lambda/l}{dt}\right)_{t\to 0} = \log(k\varepsilon_\lambda) + a\log[H_2O_2]_0 + b\log[H^+]_0 + c\log[Cr_2O_7^{2-}]_0 \tag{9}$$

Reaction orders a, b and c are obtained from the slopes of the corresponding plots $\log[d(E_\lambda/l)/dt]_{t\to 0}$ *versus* $\log[H_2O_2]_0$, $\log[Cr_2O_7^{2-}]_0$ or the *pH*, respectively. The initial rate $[d(E_\lambda/l)/dt]_{t\to 0}$ is measured at different *pH* values for either constant concentrations of dichromate with varying hydrogen peroxide concentrations, or vice versa. At $[H_2O_2] = 3 \cdot 10^{-3}$ M, the dichromate concentrations vary between $1 \cdot 10^{-3}$ M $\leq [Cr_2O_7^{2-}]_0 \leq 1 \cdot 10^{-2}$ M at each *pH* value.

Reaction order in [H_2O_2]

Figure 3 shows typical kinetic runs. The increase of $CrO(O_2)_2$ at 580 nm is given for various H_2O_2 concentrations as a function of time, whereas the respective dichromate concentration and *pH* are kept constant. From such kinetic curves, plots like $\log[d(E_{580}/l)/dt]_{t\to 0}$ *versus* $\log[H_2O_2]_0$ are obtained as shown in Fig. 4. The

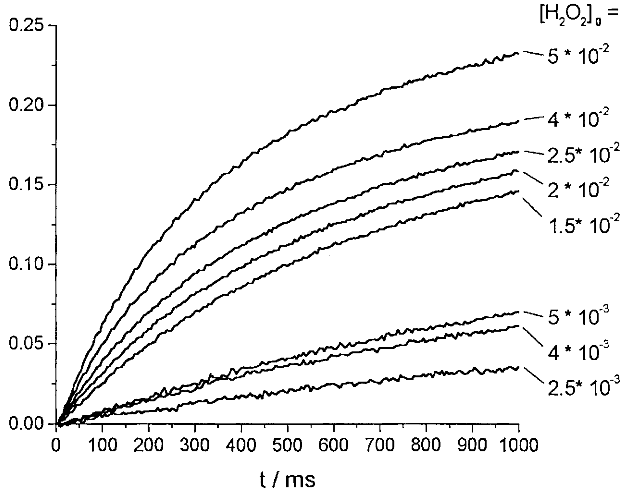


Fig. 3. Formation of $CrO(O_2)_2$, observed at 580 nm for various H_2O_2 concentrations. $[Cr_2O_7^{2-}]_0 = 2.5 \cdot 10^{-3}$ M, $pH = 2.5$ in perchloric acid

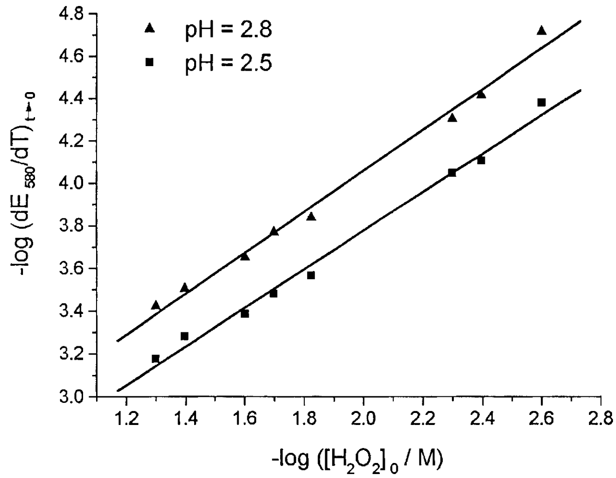


Fig. 4. Log-log plot of the initial rates of the $CrO(O_2)_2$ formation at $\lambda = 580$ nm *versus* $[H_2O_2]_0$, at $pH = 2.5$ and 2.8 in perchloric acid. Concentrations are $[Cr_2O_7^{2-}]_0 = 2.5 \cdot 10^{-3}$ M and $[H_2O_2]_0$ varying from $2.5 \cdot 10^{-3}$ M to 0.05 M. The slopes are 0.91 and 0.96, respectively

reaction order is found to be unity ($a = 1$); In perchloric, nitric and acetic acid. The dissociation of hydrogen peroxide according to:

$$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + HOO^-$$

has no influence under our experimental conditions, since its pK_a value is 11.75 [14].

pH Dependence

Within the range $2.5 \leq pH \leq 3.3$ the reaction order of $[H^+]$, c, is found as unity for perchloric, nitric and acetic acid solutions. A characteristic plot is shown in Fig. 5, where $\log[d(E_{580}/l)/dt]_{t\rightarrow 0}$ is plotted *versus pH*, using $[H_2O_2]_0 = 0.02$ M and $[Cr_2O_7^{2-}]_0 = 2.5 \cdot 10^{-3}$ M in perchloric acid.

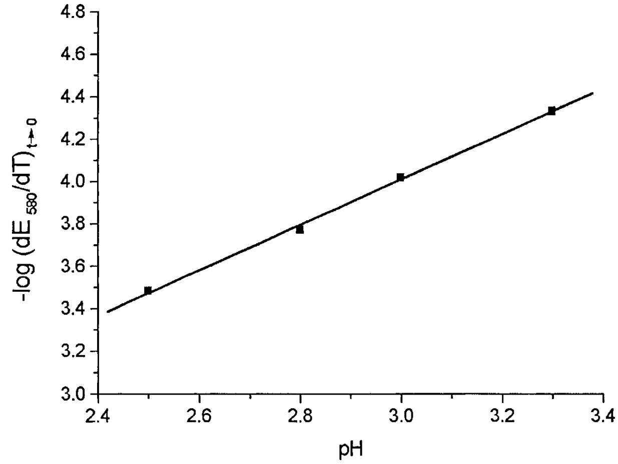


Fig. 5. Logarithm of the initial rate at $\lambda = 580\,\mathrm{nm}$ as a function of the *pH* in perchloric acid at $[Cr_2O_7^{2-}]_0 = 2.5 \cdot 10^{-3}\,\mathrm{M}$ and $[H_2O_2]_0 = 0.02\,\mathrm{M}$

Reaction order in [$Cr_2O_7^{2-}$]

In order to obtain the equilibrium concentration $[Cr_2O_7^{2-}]_{eq}$ from the initial concentration $[Cr_2O_7^{2-}]_0$, reaction (2) with $K_2 = 158\,\mathrm{M}$ must be taken into account.

$$K_2 = \frac{\left[Cr_2O_7^{2-}\right]_{eq}}{\left[HCrO_4^{-}\right]_{eq}^2} \tag{10}$$

The experimental values of the reaction order c vary between 0.43 and 0.52, indicating a reaction order of 0.5 for $[Cr_2O_7^{2-}]$. The corresponding plot of $\log[d(E_{580}/l)/dt]_{t\to 0}$ against $[Cr_2O_7^{2-}]_{0,eq}$ ranging from $5 \cdot 10^{-4}\,\mathrm{M}$ to $5 \cdot 10^{-3}\,\mathrm{M}$ is given in Fig. 6

In hydrochloric and sulfuric acid the kinetics of $CrO(O_2)_2$ formation is influenced by reactions (5) and (6), forming CrO_3Cl^- and $CrO_3(OSO_3)^{2-}$, respectively. The corresponding equilibrium constants are reported as $K_5 = 17\,\mathrm{M}^{-1}$ and $K_6 = 4.1\,\mathrm{M}^{-1}$ [10]. The change in the reaction order of $Cr_2O_7^{2-}$ from 0.5 to unity indicates an influence on the rate determining step of the reaction mechanism. If the equilibria Eqs. (5) and (6) are included in the reaction mechanism the calculated concentration of H_2CrO_4, the main reaction partner, is reduced up to a factor of 10^3. That means that the reaction with H_2O_2 gets unlikely, compared with the direct reaction of $Cr_2O_7^{2-}$ with H_2O_2 in a new rate determining step forming two peroxomonocomplex molecules $H_2CrO_3(O_2)$ under decay of $Cr_2O_7^{2-}$. Fast protonation is always established and reaction with another H_2O_2-molecule follows to form the final product $CrO(O_2)_2$.

Rate expression and rate constant

The results reported above lead to the following rate law

$$\frac{d[CrO_5]}{dt} = k[H_2O_2]\left[H^+\right]\left[Cr_2O_7^{2-}\right]^{1/2} \tag{11}$$

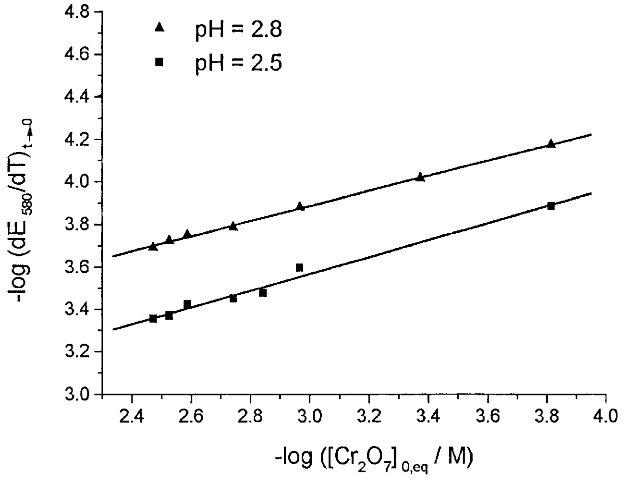


Fig. 6. Log-log plot of the initial rate at $\lambda = 580\,\mathrm{nm}$ *versus* $[Cr_2O_7{}^{2-}]$ at $pH = 2.5$ and 2.8 in perchloric acid at concentrations of $[H_2O_2]_0 = 0.02\,M$ and $[Cr_2O_7{}^{2-}]_0$ varying from $5 \cdot 10^{-4}\,M$ to $5 \cdot 10^{-3}\,M$

The square root dependence of $[Cr_2O_7{}^{2-}]$ indicates that $CrO_5 \cdot H_2O$ is not formed directly by the dichromate ion $Cr_2O_7{}^{2-}$, but in a first order reaction by $HCrO_4{}^-$. Under consideration of Eq. (2) follows:

$$\frac{d[CrO_5]}{dt} = k \cdot K_2^{1/2}[H_2O_2]\left[H^+\right]\left[Cr_2O_7{}^{2-}\right]^{1/2} \qquad (12)$$

or

$$\frac{d[CrO_5]}{dt} = k' \cdot [H_2O_2]\left[H^+\right]\left[HCrO_4{}^-\right] \qquad (13)$$

where: $[HCrO_4{}^-]_{eq} = K_2^{1/2} \cdot [Cr_2O_7{}^{2-}]_{eq}{}^{1/2}$.

To obtain the rate constant k of the formation of $CrO(O_2)_2$, the following procedure is used. From the increase of CrO_5, the observed rate constant

$$\frac{d[CrO_5]}{dt} = k_{obs}\left[Cr_2O_7{}^{2-}\right]^{1/2} \qquad (14)$$

k_{obs} is obtained at constant pH and temperature. A plot of k_{obs} *vs.* $[H_2O_2]$ results in k_1 from

$$k_{obs} = k_1[H_2O_2] \qquad (15)$$

furthermore

$$k_1 = k[H^+] \qquad (16)$$

where finally k is obtained from a plot of k_1 *vs.* $[H^+]$. The rate constant for the formation of $CrO(O_2)_2$ is found to be $k = (7.3 \pm 1.9) \cdot 10^2\,M^{-3/2}\,s^{-1}$ at $T = 293\,K$ in perchloric acid. This value is comparable to $k_L = 8.6 \cdot 10^3\,M^{-2}\,s^{-1}$ given by *Linert et al.* [20] who reported on the formation of $CrO(O_2)_2$ by $HCrO_4{}^-$ and H_2O_2, since $k_L = k\,K_2^{1/2}$ if the chromate/dichromate equilibrium is taken into account.

Proposed mechanisms

From the obtained rate law, Eq. (13), showing a third-order formation of $CrO(O_2)_2 \cdot H_2O$, several mechanisms may be envisaged. The acid dehydration of the dichromate, Eq. (2), is a permanent preequilibrium to the reaction of H_2O_2 with $HCrO_4{}^-$ or with H_2CrO_4. The overall formation of $CrO(O_2)_2 \cdot H_2O$ is than given by:

$$HCrO_4{}^- + H^+ + 2H_2O_2 \rightarrow CrO(O_2)_2 \cdot H_2O + 2H_2O \tag{17}$$

Mechanism I

Reaction starts from H_2CrO_4 appearing in acid solution by the protonation equilibrium, Eq. (4):

$$H_2CrO_4 + H_2O_2 \rightarrow H_2CrO_3(O_2) + H_2O \tag{18}$$

The formation of a *mono*peroxocomplex, $H_2CrO_3(O_2)$ in a rate determining step is followed by a another fast attack of the second H_2O_2-molecule

$$H_2CrO_3(O_2) + H_2O_2 \rightarrow CrO(O_2)_2 \cdot H_2O + H_2O. \tag{19}$$

This leads to the final diperoxocomplex $CrO(O_2) \cdot H_2O$. The reaction of $HCrO_4{}^-$ with H_2O_2 would possibly lead to $HCrO_3(O_2)^-$. By the reaction of $HCrO_3(O_2)^-$ with a second H_2O_2 molecule O^{2-} instead of OH^- would become a leaving group, which is highly unlikely. Thus the protonated species $H_2CrO_3(O_2)$ should be formed again. Within the used range of $[Cr_2O_7]_0{}^{2-}$ of $5 \cdot 10^{-4}$ M to $5 \cdot 10^{-3}$ M, and between $pH = 2.3$ to 3.3 the $[H_2CrO_4]_{eq}$ concentration varies between $1.1 \cdot 10^{-4}$ M to $2 \cdot 10^{-6}$ M, using $K_2 = 158$ M and $K_4 = 0.2$ M. These concentrations are considerable and the reaction starting with H_2CrO_4 and H_2O_2 is therefore quite likely.

Mechanism II

Theoretically, the reaction could also start from protonated $H_3O_2{}^+$, formed by:

$$H_2O_2 + H^+ \xrightleftharpoons{K_{20}} H_3O_2{}^+ \tag{20}$$

and than continue by reacting with $HCrO_4{}^-$ forming again $H_2CrO_3(O_2)$ in a rate determining step. But, with the reported protonation constant of $K_{20} = 2 \cdot 10^{-5}\,M^{-1}$ [21], the concentrations of $[H_3O_2{}^+]$ present are extremely low. Within the used range of H_2O_2 concentrations, $[H_3O_2{}^+]$ varies only between $3.2 \cdot 10^{-9}$ M to $1.6 \cdot 10^{-10}$ M at $pH = 2.3$. These concentrations make mechanism II less favourable, compared to mechanism I [22].

The formation of $CrO(O_2)_2 \cdot H_2O$ according to reaction (1) or (17) is not quantitative, but reversible. The consumption of $Cr_2O_7{}^{2-}$ does not correspond totally with the amount of $CrO(O_2)_2 \cdot H_2O$ formed. Spectrophotometrically the concentrations of $CrO(O_2) \cdot H_2O$ and $Cr_2O_7{}^{2-}$ can be followed, see Fig. 2. In aqueous solutions, both $Cr_2O_7{}^{2-}$ and $CrO(O_2)_2 \cdot H_2O$ absorb at $\lambda = 350$ nm, $E_{350} = \varepsilon_{Cr_2O_7{}^{2-}} \cdot l\left[Cr_2O_7{}^{2-}\right] + \varepsilon_{CrO_5} l\left[CrO_5\right]$. From a pure $CrO(O_2)_2 \cdot Et_2O$ solution, containing no $Cr_2O_7{}^{2-}$ ions, the extinction coefficient at $\lambda = 350$ nm could be measured. Using the known extinction coefficient for $Cr_2O_7{}^{2-}$, $\varepsilon_{350} = 3200\,M^{-2}\,cm^{-1}$, and that for $CrO(O_2)_2 \cdot H_2O$ at 580 nm, where no $Cr_2O_7{}^{2-}$

absorbs, an equilibrium constant for reaction (17) can roughly be calculated. After reaching the maximum extinction for $CrO(O_2)_2 \cdot H_2O$, constancy of $[H_2O_2]_e$ which is not detectable photometrically, is guaranteed by using $[H_2O_2]_0 = 0.02\,M$. From these results an equilibrium constant of $K_{17} \approx 4.5 \cdot 10^7\,M^{-3}$ is found for reaction (17). This is in good agreement with the reported value for $K_{17} = 5.4 \cdot 10^7\,M^{-3}$ [23].

Conclusions

The experimental rate laws for the formation of $CrO(O_2)_2$ from $Cr_2O_7{}^{2-}$ and H_2O_2 depend on the type of acid used in aqueous solutions. For perchloric, nitric, and acetic acid the reaction order in $[Cr_2O_7{}^{2-}]$ is 0.5, whereas it is unity for hydrochloric and sulfuric acid, indicating a change in the rate determining step. The reaction order is unity, for both $[H_2O_2]$ and $[H^+]$ in all cases. The most likely mechanism is the reaction of H_2CrO_4 with one H_2O_2 molecule in a rate determining step forming a monoperoxocomplex. H_2CrO_4 is formed by a protonation equilibrium with $HCrO_4{}^-$, where the latter is part of the dehydration equilibrium, according to Eq. (2). In a second, slower step the monoperoxocomplex reacts with another H_2O_2 molecule and forms the final relatively stable blue $CrO(O_2)_2 \cdot H_2O$ complex.

Experimental

Measurements were formed with a home-made stopped-flow apparatus using monochromatic wavelength or UV-VIS diode array detection. Six different syringes are available driven by air pressure [19]. The optical path length of the stopped-flow cell is $l = 3.4$ mm. Delayed flows and multi-mixing are also possible. Optical detection is performed via liquid light guides (Lumatec), either with a tungsten (12 V, 100 W) or xenon lamp (150 W) together with a monochromator. Kinetic traces are detected by a RCA photomultiplier (type: 1P 28) and stored in a Hameg digital oscilloscope (type HM 205-3) and from there transferred to a PC via HPIB for data handling. Rapid scan UV-VIS detection is recorded with a *Zeiss* diode array (type MMS UV-VIS). Registration is possible between 190 and 730 nm with 10 ms total sampling time at the shortest. The resolution is 7 nm and pixel dispersion is 2.1 nm.

All chemicals were of p.A. grade from *Merck*. Potassium salts were used for both chromium (VI) salts K_2CrO_4 and $K_2Cr_2O_7$. The concentration of H_2O_2 was determined by titration with acidic 0.1 N cerium sulphate using Ferroin (Merck) as an indicator. Different *pH* values were established by diluted solutions of HCl, H_2SO_4, HNO_3, $HClO_4$, or CH_3COOH, respectively and measured with an digital *pH* meter (type WTW, *pH* 522). $CrO(O_2)_2$ is observed at 580 nm with an extinction coefficient reported [4] as $\varepsilon_{580} = 500\,M^{-1}\,cm^{-1}$. The *pH* was varied in the range of $2.5 \leq pH < 3.3$. Below $pH = 3.3$, the signal intensity of $CrO(O_2)_2$ was too low to be detected. For all measurements the temperature was $T = 293 \pm 2\,K$. The equilibrium concentrations of $[Cr_2O_7{}^{2-}]_{eq}$ and $[HCrO_4{}^-]_{eq}$ were calculated from Eqs. (3) and (4) and from the initial concentration $[Cr_2O_7{}^{2-}]_0$ as: $[Cr_2O_7{}^{2-}]_{eq} = [Cr_2O_7{}^{2-}]_0 - \frac{1}{2}[HCrO_4{}^-]_{eq}$.

Acknowledgements

G. Grampp and S. Landgraf would like to thank the Austrian Academic Exchange Service (ÖAD) and the Austrian Federal Ministry of Education, Science and Culture for financial support. T. Wesierski, B. Jankowska, D. Sabou, E. Kalisz and B. Mladenova express their grateful thanks to the CEEPUS program of the Austrian Federal Ministry of Education, Science and Culture and the ÖAD for scholarships and financial support.

References

[1] Jander G, Blasius E (1969) Lehrbuch der analytischen und präparativen anorganischen Chemie. S. Hirzel, Stuttgart, p 228

[2] a) Schwarz R, Giese H (1932) Ber. **65**: 871; b) Truck DG, Walters RM (1962) J Chem Soc (London) 3948

[3] Cotton F, Wilkinson G (1968) Anorganische Chemie. 2nd ed. VCH-Weinheim p 777

[4] Griffith WP (1962) J Chem Soc (London) 3948

[5] Ciminale F, Camporeal M, Mello R, Troisi L Corei R (1989) J Chem Soc Perkin Trans 2 417

[6] Curci R, Giannattasio S, Scieacoveli S, Troisi O, Troisi L (1984) Tetrahedron **40**: 2763

[7] Mousari MF, Firozabadi H, Shamsipur M (1994) Int J Chem Kin **26**: 497

[8] Khodaei MM, Jamali AA (2000) J Sci I R Iran **11**: 105

[9] Haight Jr. GP, Richardson DC, Coburn NH (1964) Inorg Chem 3: 1777

[10] Tong JY, King EL (1953) J Am Chem Soc **75**: 6180

[11] Kepert DL (1973) Comp Inorg Chem **4**: 607

[12] Neuss JD, Riemann WJ (1956) J Am Chem Soc **56**: 2238

[13] Howard JR, Nair VSK, Nancollas GH (1958) Tans Faraday Soc **54**: 1034

[14] Turnay TA (1965) Oxidation Mechanisms. Butterworth, London

[15] See Ref. [14], page 124. There is as misprint in K there. The reported $K = 0.18\,\mathrm{M}^{-1}$ should read K^{-1} for the corresponding equilibrium given

[16] Westheimer FH (1949) Chem Rev **45**: 419

[17] Waters WA (1958) Quart Rev Chem Soc Lond **12**: 177

[18] Brown SB, Jones P, Sugget A (1970) Prog Inorg Chem **13**: 159

[19] Nickel U, Kemnitz K, Jaenicke W (1978) J Chem Soc Perkin 2 1188

[20] El-Ayaan U, Reisacher R, Linert W (1999) J Chem Res Synop **521**(9): 2256

[21] Evans MG, Uri N (1949) Trans Faraday Soc **45**: 224

[22] Orhanović M, Wilkins RG (1967) J Am Chem Soc **89**: 278

[23] Moore P, Kettle SFA, Wilkins RG (1966) Inorg Chem **5**: 466

Verleger: Springer-Verlag KG, Sachsenplatz 4–6, A-1201 Wien. – Herausgeber: Österreichische Akademie der Wissenschaften, Dr.-Ignaz-Seipel-Platz 2, A-1010 Wien, und Gesellschaft Österreichischer Chemiker, Eschenbachgasse 9, A-1010 Wien. – Redaktion: Währinger Straße 38, A-1090 Wien. – Satz und Umbruch: Thomson Press Ltd., Chennai, India. – Offsetdruck: Manz Crossmedia, A-1051 Wien. – Verlagsort: Wien. – Herstellungsort: Wien. – Printed in Austria.