



Review

On the peroxomolybdate complexes as sources of singlet oxygen

László J. Csányi*

Department of Inorganic and Analytical Chemistry, University of Szeged, P.O. Box 440, H-6701 Szeged, Hungary

ARTICLE INFO

Article history:

Received 9 November 2009
 Received in revised form 10 February 2010
 Accepted 10 February 2010
 Available online 18 February 2010

Keywords:

Peroxomolybdenum(VI) complexes
 Mo(VI) catalysis
 Triperoxomolybdate oxidant
 H_2O_2 dismutation
 $^1\text{O}_2$ formation

ABSTRACT

The successive formation of peroxomolybdenum(VI) complexes is discussed and it is shown that proton-consuming steps are followed by a proton-producing one; the pH maximum (=10) appears at a $[\text{H}_2\text{O}_2]/[\text{MoO}_4]^{2-}$ ratio of 2:1. The approximated formation constants are utilized to calculate the concentrations of peroxo complexes as a function of the ligand concentration. The mono-, di- and tetraperoxo complexes are formed in only negligible quantities, whereas the oxodiperoxohydroperoxo (simply, triperoxo) complex proves to be the predominant species. The triperoxo complex may react directly if a sufficiently reactive partner is present; if not, it oxidizes H_2O_2 to $^1\text{O}_2$, which reacts further. The activation parameters of formation of O_2 are determined as a function of pH: the enthalpy minimum ($50.45 \text{ kJ mol}^{-1}$) is found at pH 10, where the negative activation entropy reaches its lowest value ($-149.5 \text{ J K}^{-1} \text{ mol}^{-1}$). The possible functions of the peroxo ligands are considered.

© 2010 Elsevier B.V. All rights reserved.

Contents

1. Introduction	1
2. Experimental and methods	1
3. Results and discussion	1
3.1. Spectrophotometric detection of triperoxomolybdate in dilute aqueous solution	3
3.2. The triperoxomolybdate complex is sole source of $^1\text{O}_2$ formation	3
3.3. Role of triperoxomolybdate in formation of $^1\text{O}_2$ and some closing comments	4
4. Conclusions	5
Acknowledgements	6
References	6

1. Introduction

This paper presents a brief survey of the data currently available on the peroxo derivatives of Mo(VI), including recent results, and draws attention to some unanswered questions in connection with some d_0 metalate-catalysed oxidations by H_2O_2 .

2. Experimental and methods

Aldrich extrapure reagents were used. Measurements on the decompositions of the peroxomolybdenum(VI) complexes were carried out by gas volumetry with a slightly modified Metrohm E 415 Multi-Dosimat gas burette. The reactor was connected via a switching manometer filled with 10% H_2SO_4 , which helped to

maintain the internal pressure automatically at atmospheric level. The decompositions were followed in parallel by absorption spectrophotometry at 450 nm.

3. Results and discussion

It was observed by Muthmann and Nagel [1] that monoperoxomolybdates, M_2MoO_5 , are formed when a moderate quantity of H_2O_2 is reacted with alkali metal molybdates. This finding was confirmed by Martinez [2], although it had earlier been reported by Jahr [3a,b] that, in weakly acidic or neutral solution, the molybdate ion is immediately transformed by H_2O_2 into a yellowish oxohydrodiperoxo complex, HMoO_6^- , with a simultaneous increase in pH.

In the early 1930s, it was described by Gleu [4], Rosenheim et al. [5] and Kobosev and Sokolow [6] that a reddish-brown tetraperoxomolybdate complex is also formed when H_2O_2 is applied in a considerable excess. This complex was similarly mentioned in the

* Tel.: +36 62 544000x3574; fax: +36 62 420505.
 E-mail address: [ljcsanyi@chem.u-szeged.hu](mailto:ljscanyi@chem.u-szeged.hu).

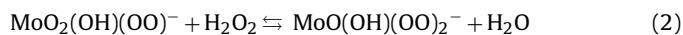
paper by Jahr [3a,b], but without any reference to the earlier [4–6] authors.

It was later observed by Csányi [7] that, when H_2O_2 is added in small portions to nearly neutral alkali metal molybdate solutions, the pH initially progressively increases. As the H_2O_2 addition is continued, however, the pH eventually starts to decrease. The maximum pH (=10) is observed at a concentration ratio $[\text{H}_2\text{O}_2]/[\text{MoO}_4^{2-}] = 2:1$, which means that, up to completion of the formation of diperoxomolybdenum(VI) complex, this peroxidation is a proton-consuming process. It has been considered that the entering H_2O_2 attacks at one face of the tetrahedron of the molybdate ion and forms a weakly bonded intermediate [8]. Addition of a proton (see Eq. (1)) to one of the oxo groups of the intermediate then lengthens the Mo–O bond and strengthens the Mo–ligand bond, thereby lowering the energy of activation required to form an activated complex with an expanded coordination sphere. The rate-determining step may involve both the configuration change and the bond formation. If one of the coordinated H_2O molecules of the hydrated molybdate ion furnishes the proton for the protonation of the oxo group, an OH^- ion will simultaneously be released and the pH of the solution will increase:



The formation constant, $K_{1:1}$ was found to be $(9.12 \pm 0.67) \times 10^{-7}$ [9]. The conclusion of Jahr [3a,b] should be corrected in that the proton-consuming peroxidation occurs already on the entry of the first ligand molecule.

The next step of the peroxidation, the formation of the oxohydroxidoperoxo complex, does not induce further pH change:



The formation constant, $K_{2:1}$, was found to be $(2.68 \pm 0.17) \times 10^5$ [9].

It should be mentioned that the acid form of diperoxomolybdenum(VI) has been prepared [10] by the passage of alkaline solution of the components through a Dowex 50 cation-exchange resin column, in R–H form; the acidity constants were determined potentiometrically to be $K_1 = 3.0 \times 10^{-3}$ and $K_2 = 7.94 \times 10^{-10}$.

The subsequent step of peroxidation is a proton-producing reaction. The initially light-yellow solution starts to assume a faint brownish tint when the concentration ratio $[\text{H}_2\text{O}_2]/[\text{MoO}_4^{2-}]$ reaches 1.6–1.8, and becomes a stronger reddish-brown when H_2O_2 is applied in a considerable excess [9].

The preparations of the pyridinium salts of the mono-, di- and triperoxomolybdenum(VI) complexes in the solid state were described by Beiles et al. [11]. An attempt was made to isolate such large complex anions by precipitating them as salts of equally large counter-cations. This favours the stability of the crystalline state relative to the solution and makes it easier to obtain crystals of the desired complex, for the lattice energy is inversely proportional to the sum of the radii: $U = f(1/(r_+ + r_-))$, whereas the enthalpy of hydration is the sum of two quantities inversely proportional to the individual radii, $\Delta H_{\text{hyd}} = f_1(1/r_+) + f_2(1/r_-)$ [12]. The successful preparation methods were as follows [11]:

(pyH)₂MoO₆: 50 dm³ of 20% H_2O_2 was added to 20 g of ammonium molybdate, and the resulting solution was treated with 11 g of pyridine in 100 dm³ of water, and then acidified with 2 N H_2SO_4 until a precipitate appeared (pH 3–5). Pale greenish-yellow glistening prisms were formed.

(pyH)₂MoO₇: freshly prepared (pyH)₂MoO₆ was dissolved in small portions in a tenfold excess of 30% H_2O_2 at 3–5 °C. The filtrate was evaporated in a current of air, and the

resulting large greenish-yellow crystals were washed with acetone.

(pyH)₂MoO₅ the monoperoxo complex was obtained by partial oxidation of (pyH)₂MoO₆ solution with permanganate.

These important findings were subsequently somewhat neglected for a rather long time. In spite of a successful preparation of triperoxomolybdate (the tungsten product had a 2.5:1 peroxide:metal ratio), Griffith [13] claimed that “there is little evidence for the existence of true 3:1 permolybdates and pertungstates”. . . “it seems likely from the chemical properties and analyses that they simply contain molecules of hydrogen peroxide of crystallisation”. His doubt perhaps arose from the fact that the existence of the triperoxo species in dilute aqueous solution was not supported by Raman and IR spectrometry.

Some years later, the X-ray crystal structures of the dimer salts $(\text{pyH}^+)_2[\text{O} < \{\text{MoO}(\text{OO})_2(\text{H}_2\text{O})\}_2]^{2-}$ and $(\text{pyH}^+)_2\{\text{MoO}(\text{OO})_2 > \text{OOH}\}_2^{2-}$ with –O– and >OOH bridges were described in a short note by Mitschler et al. [14] and then in detail by Le Carpentier et al. [15]. It was emphasized by the latter authors that the oxodiperoxo complex is decomposed very slowly at room temperature, but the triperoxo complex loses its O_{act} content quite quickly. Despite these significant and confirmed findings, the opposition [13] was withdrawn only later, when the Raman and IR investigations of the peroxo complexes were complemented by ⁹⁵Mo NMR and ¹⁸³W spectrometry [16]. It is surprising, however, that the subsequent papers [17–20] questioned or ignored the triperoxo complex identified earlier in the solid state [11,14,15] and in solution [9].

During the period when interest in singlet oxygen chemistry was growing, a valuable screening study by Aubry [21] attracted particular attention to the chemistry of the peroxo derivatives of Mo(VI). It was demonstrated that the molybdate-catalysed dismutation of H_2O_2 is a quantitative source of ¹O₂.

Aubry and Cazin concluded in [17] that the dismutation of H_2O_2 occurs through a dioxodiperoxomolybdate anion, MoO_6^{2-} . The reaction was found to be first order with respect to MoO_4^{2-} , second order at low H_2O_2 concentration, and zero order at concentrations higher than 0.1 mol dm⁻³. The pH dependence and the stoichiometry of decomposition were investigated in the presence of RTC (tetrapotassium rubrene-2,3,8,9-tetracarboxylate) as ¹O₂ trap and the rate maximum was found at pH 10.5.

The initial statements in [17], however, are in contradiction with the earlier observations of Le Carpentier et al. [15], who observed that the dioxodiperoxo complex is decomposed very slowly at room temperature, whereas the triperoxo complex loses its O_{act} content quite quickly. Aubry et al. [18] emphasized that the protonated ion HMoO_6^- becomes inactive for ¹O₂ production. They stated that the naphthalenic endoperoxides serve as useful chemical sources of ¹O₂ at moderate temperature (30–50 °C).

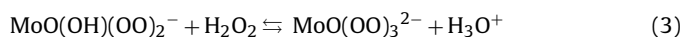
Lydon et al. [22] investigated the kinetics of formation and dissociation of the peroxo complexes in acidic perchlorate solution with a stopped-flow method, and found that the entry of the second peroxo ligand is rate-determining in the formation of the oxodiperoxomolybdenum(VI) complex. They observed that the hydrolysis of $\text{MoO}(\text{OO})_2$ to $\text{MoO}(\text{OH})(\text{OO})_2^-$ proceeded with an equilibrium constant of 0.014.

A further, similarly important contribution to the chemistry of peroxomolybdenum(VI) was the finding by Schwane and Thompson [23] of an unusual rate law for the formation of oxodiperoxomolybdenum(VI): the H_2O_2 concentration was of second order at $[\text{H}^+] \geq 0.1$ mol, but of first order at $[\text{H}^+] \leq 0.003$ M. This means that the entry of the second H_2O_2 molecule is rate-determining in the former case, whereas the entry of the first H_2O_2 is limiting in the latter case. This can be regarded as direct proof

of the stepwise formation of peroxomolybdate complexes, but also indicative of the transitory formation of the monoperoxo derivative, $\text{Mo}(\text{O})_2(\text{OH})(\text{OO})^-$. The latter could not be detected as it is unstable, and the higher peroxo complexes are formed very quickly even at lower ligand concentration. It should be noted that Thompson's group later succeeded in precipitating $\text{MoO}_2(\text{OH})(\text{OO})^-$ ion through use of the chelating agents 2,6-pyridinedicarboxylate and nitrilotriacetate as heteroligands [24].

3.1. Spectrophotometric detection of triperoxomolybdate in dilute aqueous solution

The series of absorption spectra of Mo(VI) recorded in the presence of increasing concentrations of H_2O_2 at pH 7 reveal only one peroxide species at the maximum of 310 nm (and an isobestic point at 253 nm): oxohydroxodiperoxomolybdenum(VI) [9]. In H_2O_2 -rich molybdate solution, a new maximum is formed at 450 nm, that of the red-brown tetraperoxomolybdate (see Eq. (4), below). Variation of the concentration ratio $[\text{H}_2\text{O}_2]/[\text{MoO}_4^{2-}]$ from 9 to 100 at pH 10 is accompanied by a considerable change in the absorbance ratio A^{380}/A^{450} , from 15.6 to 0.3, and the maximum at 450 nm is never reached; instead, a monotonously rising absorption curve is obtained towards shorter wavelengths. The molar absorbance of the oxohydroxodiperoxo species at 380 nm at pH 7 is $78.2 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, but it decreases appreciably as the pH increases. It was concluded from this that, besides $\text{MoO}(\text{OH})(\text{OO})_2^-$, a more strongly coloured species must also be present in the solution to account for the higher absorbance observed at 380 nm. This is logically oxotriperoxomolybdate, $\text{MoO}(\text{OO})_3^{2-}$ [9]. These spectrophotometric observations prove that $\text{MoO}(\text{OO})_3^{2-}$ is indisputably present in dilute solutions too:

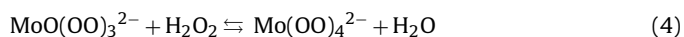


The formation constant, $K_{3,1}$, was found to be $(1.26 \pm 0.06) \times 10^6$. Reaction (3) explains the slowing-down of the increase, followed by a decrease in the pH as the concentration ratio $[\text{H}_2\text{O}_2]/[\text{MoO}_4^{2-}]$ approaches and surpasses 2 [9].

At the same time, Griffith's group [16] furnished support for formation of the triperoxo species by means of ^{95}Mo and ^{183}W NMR spectrometry. They established that the principal species are $[\text{M}(\text{OO})_4]^{2-}$, $[\text{M}(\text{OO})_3]^{2-}$, $[\text{M}_2\text{O}_3(\text{OO})_4(\text{H}_2\text{O})_2]^{2-}$ ($\text{M} = \text{Mo}$ or W) and, at lower pH, complexes containing the $[\text{M}(\text{OO})]^{2+}$ unit. Parallel studies on the catalytic oxidation of alcohols and alkenes in an excess of H_2O_2 in the pH range 0.5–7 suggest that $[\text{M}_2\text{O}_3(\text{OO})_4(\text{H}_2\text{O})_2]^{2-}$ is the most effective oxidizing species.

The findings of Aubry et al. [17] were confirmed by Böhme and Brauer [19] by measurement of the infrared phosphorescence of $^1\text{O}_2$ at 1270 nm. They established that in the concentration range $0.1 < [\text{H}_2\text{O}_2] < 0.3 \text{ mol dm}^{-3}$ di- and tetraperoxo-molybdenum(VI) complexes are formed, but the latter does not contribute significantly to $^1\text{O}_2$ formation. On the other hand, the similar investigations by Niu and Foote [20] showed that $^1\text{O}_2$ was produced during the decomposition of the freshly dissolved tetraperoxo derivatives, but they did not consider that the less stable tetraperoxo complex decomposes through the partial loss of ligands during dissolution and $^1\text{O}_2$ is released by the lower complex.

The final peroxidation step is the formation of tetraperoxo-molybdenum(VI):



The best least squares fit was for $K_{4,1} = 1.58 \pm 0.02$ [9]. There is another possibility for formation of the tetraperoxo complex: on the action of alkali, oxohydroxodiperoxo-molybdate may undergo dismutation:

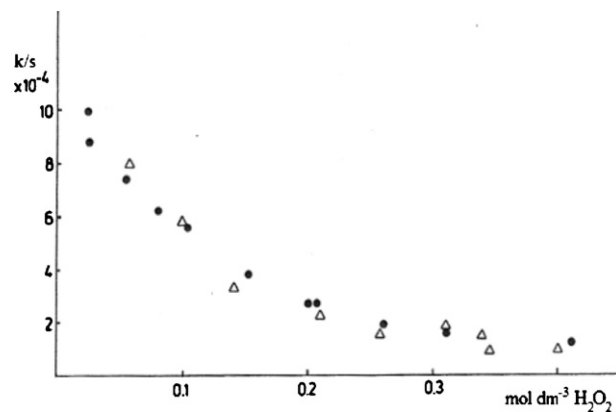
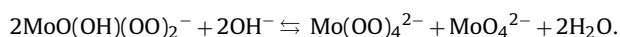


Fig. 1. Dependence of the rate coefficient of the Mo(VI)-catalysed dismutation of H_2O_2 on the ligand concentration. Conditions: $0.005 \text{ mol dm}^{-3} \text{ Na}_2\text{MoO}_4$, 0.18 mol dm^{-3} phosphate buffer, $0.005 \text{ mol dm}^{-3}$ EDTA, pH 10.5, 298 K; (●) values obtained by gasvolumetry; (Δ) values obtained by spectrophotometry at 450 nm.

The tetraperoxo complex exhibits distorted tetrahedral (slightly disphenoidal) geometry, in which the bidentate peroxo ligands deviate from the isosceles triangular structure in consequence of the greater interaction of the oxygen 2s orbital (axial > equatorial) with the molybdenum p_z orbital [25]. Such deviations of bidentate peroxo ligands from the isosceles triangular structure are observed for all the peroxo derivatives of the other d_0 transition metals [26].

3.2. The triperoxomolybdate complex is sole source of $^1\text{O}_2$ formation

Mention must be made of a lecture delivered by Thompson [27a,b] at the 14th Conference on Coordination Chemistry (7–11 June 1993, Smolenice, Slovakia), in which it was first announced that the triperoxo complex is alone responsible for the formation of $^1\text{O}_2$, significant contributions from other peroxo complexes being completely precluded. This conclusion was supported by sensitive calorimetric and ^{95}Mo NMR measurements.

Some months later (14 October 1993) the present author gave a talk at the jubilee session of the Hungarian Academy of Sciences on the occasion of the 85th birthday of Professor Zoltán G. Szabó, in which he presented a similar statement about the role of the triperoxo complex, supported by two figures (the talk was delivered and published in Hungarian [28]). Fig. 1 depicts the rate coefficient of the molybdate-catalysed decomposition of H_2O_2 as a function of the ligand concentration in the $[\text{H}_2\text{O}_2]/[\text{MoO}_4^{2-}]$ range of 5–80. The points denoted by (●) and those by (Δ) were calculated from the volume of O_2 evolved, and from the light absorption change measured at 450 nm, respectively. It is clearly seen that the two types of measurements yielded almost identical data. The rate coefficient decreased considerably on increase of the ligand concentration. At a higher ligand excess, however, the rate coefficient dropped to close to the low value for the self-decomposition of H_2O_2 observed in the absence of molybdate. This observation reinforced the earlier finding of Böhme and Brauer [19] that decomposition of the tetraperoxomolybdate species does not contribute significantly (in our observations not at all) to the molybdate-catalysed dismutation of H_2O_2 . It should be mentioned, however, that it was used in [28] at a molybdenum(VI) concentration five times higher than reported by Böhme and Brauer (see Fig. 2 in [19]).

The Arrhenius parameters of the molybdate-catalysed decomposition of H_2O_2 as a function of pH are presented in Fig. 2. The changes in activation enthalpy, ΔH^\ddagger , and entropy, ΔS^\ddagger , are denoted by x and ●, respectively. It is seen that ΔH^\ddagger decreases with increasing pH and reaches its minimum, $57.17 \text{ kJ mol}^{-1}$, at pH 10,

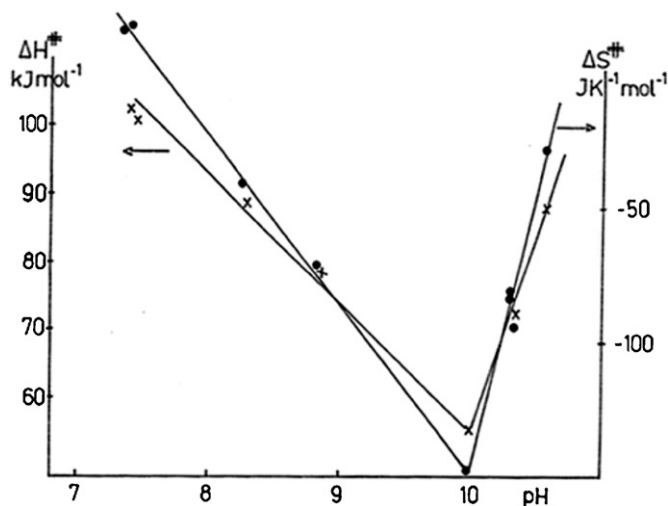


Fig. 2. Dependence of the Arrhenius parameters of the Mo(VI)-catalysed dismutation of H_2O_2 on the pH. Conditions: $0.0068 \text{ mol dm}^{-3} \text{ Na}_2\text{MoO}_4$, $0.080 \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$, 0.09 mol dm^{-3} phosphate buffer; (x) ΔH^\ddagger ; (•) ΔS^\ddagger .

increasing sharply at higher pHs. The change in ΔS^\ddagger displays a similar tendency. Between pH 7 and 10, the initially small positive value becomes negative, reaches its minimum, $-149.5 \text{ JK}^{-1} \text{ mol}^{-1}$, at pH 10, and then increases steeply in response to pH increase. In our view, the observed minimum in ΔH^\ddagger and the fairly large negative ΔS^\ddagger are probably connected with the rearrangement of the coordination sphere of Mo(VI) into the mixed ligand triperoxo complex $\text{Mo}(\text{OO})_2(\text{OOH})^-$, which is formed by a condensation of H_2O_2 with the precursor $\text{Mo}(\text{OO})_2(\text{OH})^-$.

The concentration data presented in Table 1 were computed from the formation constants of the peroxomolybdenum(VI) complexes, obtained earlier by means of spectrophotometry [9] (conditions: $0.005 \text{ mol dm}^{-3} \text{ Na}_2\text{MoO}_4$, room temperature, pH 10). For comparison, Table 1 contains the data of Nardello et al. [29] (obtained by ^{95}Mo NMR spectrometry at $1.0 \text{ mol dm}^{-3} \text{ Na}_2\text{MoO}_4$, 0°C , natural pH; $K_1 = 1.5 \times 10^2$, $K_2 = 1.2 \times 10^3$, $K_3 = 2.1 \times 10^2$, $K_4 = 1.4 \pm 0.1$). It should be emphasized that both proton-consuming and proton-producing processes during the peroxidation of Mo(VI) were discussed by Csányi et al. [9], though they were rejected by Nardello et al. [29] as some of the data in their argument differed from those in [9] (e.g. $K_{2:2}$ was never used, while $K_{3:1}$ was 1.26×10^6 and not 1.26×10^{-8}). The distribution data obtained indicate that the mono-, di- and

tetraperoxo complexes are formed in only relatively low quantities, the triperoxo complex proving to be the predominating species. At low metal concentration ($0.005 \text{ mol dm}^{-3}$), the concentration maximum for $\text{MoO}(\text{OO})_3^{2-}$ was observed only at higher ligand concentrations (4 and 15 times higher, respectively) than expected, but at $1.0 \text{ mol dm}^{-3} \text{ MoO}_4^{2-}$ the maximum is obtained at the expected $3.0 \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$ in both cases.

3.3. Role of triperomolybdate in formation of $^1\text{O}_2$ and some closing comments

It was recently shown by Nardello et al. [30] that the oxidation of tiglic acid ($\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{CO}_2\text{H}$) follows different pathways in the Mo(VI)- H_2O_2 system when the pH of the reacting solution is altered under similar conditions of temperature and concentration. In deuterated water at $\text{pD} \leq 7.2$, 2-epoxy-2-methylbutanoic acid and a little diol were produced. The same epoxo derivative was obtained when tiglic acid was oxidized with a potassium tetraperoxomolybdate preparation in H_2O at $\text{pH} = 5.4$, whereas in aqueous alkaline medium tiglic acid was transformed into 3-hydroperoxy-2-methylenebutanoic acid. In our opinion, in each case the triperoxomolybdate complex is the true oxidizing reagent. In acidic medium, the $\text{MoO}(\text{OO})_2(\text{OOH})^-$, like other peroxy acids, behaves as a reactive epoxidizing agent, probably reacting according to the Sharpless mechanism ([26], and [30] in 1,3,4,7 papers cited therein). In alkaline medium, the $-\text{OOH}$ ligand of the triperoxo complex starts to deprotonate [10,17] and peroxidation of the tiglate is performed by $\text{Mo}(\text{O})(\text{OO})_3^{2-}$, producing $^1\text{O}_2$, which is inserted into the $\text{CH}-$ group of the reagent.

The oxidations of certain hydrophobic organic substrates (rubrene, diphenyl-anthracene, tetracyclone, α -terpine, dibenzyl and diphenyl sulfide, etc.) were investigated by Aubry and Boutemy [31] in reverse microemulsions (water in oil) with chemically generated $^1\text{O}_2$ (Mo(VI)-catalysed dismutation of H_2O_2) and with flash photolysis. The latter studies demonstrated that in such media $^1\text{O}_2$ exhibits kinetic behaviour similar to that observed under homogeneous conditions. It was shown that only sufficiently reactive compounds can be completely oxidized by this method; the lifetime of $^1\text{O}_2$ in microemulsion was found to be $42 \mu\text{s}$, while in water it was only $4.4 \mu\text{s}$.

The $\text{MO}_4^{2-}-\text{H}_2\text{O}_2$ systems were also investigated by Nardello et al. [32] by reacting $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{MO}_4$ ($\text{M} = \text{Mo}$ and W) with $0.6 \text{ mol dm}^{-3} \text{ H}_2\text{O}_2$ at $\text{pH} \geq 10$ and measuring the time dependence of the luminescence of the $^1\text{O}_2$ formed in the absence of reducing partners. The luminescence maximum was observed at 20 min in the tungstate system, and at 2 min in the molybdate system. Stud-

Table 1
Products of peroxidation of molybdenum(VI) as a function of ligand concentration, calculated using the cumulative β constants, in mol dm^{-3} and %.

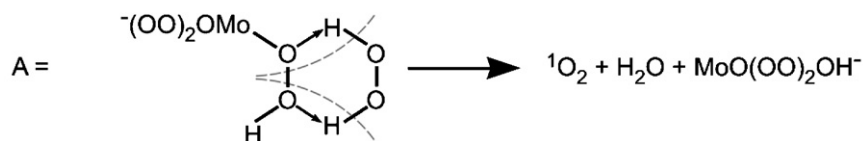
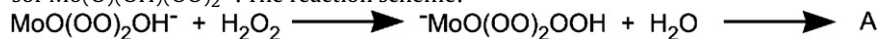
L	Csányi et al. [9]				Nardello et al. [29]			
	$\text{H}_1\text{M}_1\text{L}_1$	$\text{H}_1\text{M}_1\text{L}_2$	$\text{H}_0\text{M}_1\text{L}_3$	$\text{H}_0\text{M}_1\text{L}_4$	$\text{H}_0\text{M}_1\text{L}_1$	$\text{H}_0\text{M}_1\text{L}_2$	$\text{H}_0\text{M}_1\text{L}_3$	$\text{H}_0\text{M}_1\text{L}_4$
0.0050	8.293-09 1.65-04%	5.928-07	1.574-03	6.477-07	6.266-04 12.6%	1.033-03	2.982-04	5.737-07
0.010	6.857-09	7.670-07 1.53-02%	3.188-03	2.052-06	5.969-04	1.854-03	1.008-03	3.654-06
0.015	2.339-09	5.438-07	4.690-03	6.282-06	3.876-04	2.075-03 41.51%	1.945-03	1.215-05
0.020	7.847-11	1.023-07	4.961-03 98.22%	3.723-05	1.986-04	1.785-03	2.809-03	2.947-05
0.025		5.086-08	4.920-03	7.387-05		1.405-03	3.378-03	5.412-05
0.070							4.290-03	3.225-04
0.075							4.293-03 85.86%	3.517-04
0.080							4.292-03	3.806-04

Conditions: $0.005 \text{ mol dm}^{-3} \text{ Na}_2\text{MoO}_4$, pH 10.0, $0.005 \text{ mol dm}^{-3} \text{ EDTA}$, 298 K; $\text{H}_1\text{M}_1\text{L}_1 = \text{MoO}_2(\text{OH})(\text{OO})^-$, $\text{H}_1\text{M}_1\text{L}_2 = \text{MoO}(\text{OH})(\text{OO})_2^{2-}$, $\text{H}_0\text{M}_1\text{L}_3 = \text{MoO}(\text{OO})_3^{2-}$, $\text{H}_0\text{M}_1\text{L}_4 = \text{Mo}(\text{OO})_4^{2-}$, $\text{H}_0\text{M}_1\text{L}_1 = \text{MoO}_3(\text{OO})^{2-}$, $\text{H}_0\text{M}_1\text{L}_2 = \text{MoO}_2(\text{OO})_2^{2-}$, $\log \beta_1$ [9] = 7.96, β_2 [9] = 13.39, β_3 [9] = 10.39, β_4 [9] = 10.58, $\log \beta_1$ [29] = 2.176, β_2 [29] = 5.255, β_3 [29] = 7.577; β_4 [29] = 7.723 and for both computations the acid dissociation exponent of H_2O_2 , $\log \beta_5 = -11.6$, was used.

ies of the pH dependence of $^1\text{O}_2$ formation with use of the RTC trap further revealed that the maximum appeared at pH 10.5 in both systems. Accordingly, these systems behave very similarly in many ways, but the tungstate catalysis is considerably slower. However, ^{183}W NMR spectroscopy indicated only mono-, di- and tetraperoxo complexes; triperoxo species were not detected at all. The absence of the triperoxo signal was explained in that diperoxotungstate is converted directly into tetraperoxotungstate, which was found to be much more stable than the diperoxomolybdate. It was therefore concluded that the main precursor of $^1\text{O}_2$ here is diperoxotungstate [32]. If we accept this explanation, then we have to account for how the disproportionation of diperoxometalate complexes takes place: how and why one of the bidentate OO^{2-} ligands behaves as an oxidizing agent, and the other as a reductant. Another question that emerges is why the conversion of the diperoxo complex into tetraperoxotungstate is so fast, in spite of the fact that, according to the explanation, it could occur only in trimolecular collisions. It would be a more logical conclusion that ^{183}W NMR spectrometry is not sensitive enough for the observation of the triperoxotungstate species formed in such a low concentration, $k_{3\rightarrow 4}$ probably being larger than $k_{2\rightarrow 3}$. Otherwise, Fig. 8 (a plot of equilibrium (13): $\{\text{WO}_n(\text{OO})_{4-n} + n\text{H}_2\text{O}_2 \rightleftharpoons \text{W}(\text{OO})_4^{2-} + n\text{H}_2\text{O}\}$ according to Eq. (15)) in the paper [32] (Supporting Information) may furnish experimental support for the foregoing conclusion. The calculated slope (n) is here 1.92 rather than 2.0, which means that, besides $\text{WO}_2(\text{OO})_2^{2-}$, some $\text{WO}(\text{OO})_3^{2-}$ complex was also formed, resulting in a lowering of the number of $(\text{H}_2\text{O}_2)_{\text{free}}$ molecules exchanged at equilibrium (13). Triperoxotungstate was likewise prepared by Beiles et al. [11]; its very similar behaviour to that of the molybdenum system strongly supports the above conclusion.

The MoO_4^{2-} - H_2O_2 system is known to behave as a fairly strong oxidizing agent, probably because of the presence of the perhydroxyl ligand in the triperoxo complex [14,15]. This is considerably more active than uncomplexed H_2O_2 , its activity approaching those of peroxomonosulfuric (Caro's) acid ($E^0 = 1.842\text{ V}$ [33]) and some organic peroxy acids. Bromide ion is rapidly oxidized to bromine in acidic solutions. It should be noted, however, that the Br^-/Br_2 test is positive in slightly acidified $\geq 30\%$ H_2O_2 solutions too, in which the formation of the perhydroxyl ion containing adduct is conceivably due to the autodissociation of H_2O_2 : $\text{H}_2\text{O}_2 + \text{H}_2\text{O}_2 \rightleftharpoons \{\text{H}_3\text{O}_2^+ \cdot \text{OOH}^-\}$.

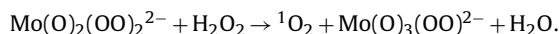
The question arises of whether the rapid oxidation of bromide ion (and other oxidizable substrates) is due to the immediate appearance of the HOO^- group in the mixed ligand triperoxomolybdenum(VI) complex, or to the $^1\text{O}_2$ which is probably formed during a further reaction of H_2O_2 with the mixed ligand complex. It is thought that this event depends on the reactivity of the reducing partner. If the partner is quite reactive, then the HOO^- ligand reacts immediately. If the partner is not reactive enough, then the mixed ligand triperoxo complex will react first with H_2O_2 in excess via H-bond interactions of the O-atoms of the HOO^- ligand of triperoxomolybdate. Thereby, a six-membered transition adduct (A) is formed, which quickly disintegrates into $^1\text{O}_2$, H_2O and the precursor $\text{Mo}(\text{O})(\text{OH})(\text{OO})_2^-$. The reaction scheme:



In such cases, the reductants will presumably be oxidized by the $^1\text{O}_2$ formed.

It should be noted that [29] mentions an analogous but (in my opinion) less probable reaction of H_2O_2 with oxidiperoxomolyb-

date:



The monomolecular decomposition of triperoxomolybdate was similarly assumed as a possible source, $\text{Mo}(\text{O})(\text{OO})_3^{2-} \rightarrow ^1\text{O}_2 + \text{Mo}(\text{O})_3(\text{OO})^{2-}$, and decomposition of the diperoxomolybdate [17,18], $\text{Mo}(\text{O})_2(\text{OO})_2^{2-} \rightarrow ^1\text{O}_2 + \text{MoO}_4^{2-}$, was rejected.

Further, it does not seem at all probable that one (or both) of the bidentately bound OO^{2-} ligands of $\text{MoO}_2(\text{OO})_2^{2-}$ is protonated to give HOO^- group(s) in slightly acidic medium, this being the explanation of the bromide test. The positive Br^-/Br_2 test is due to the characteristic behaviour of the systems of molybdate (and tungstate and vanadate) with H_2O_2 . As a counter-example, the behaviour of the peroxotitanium(IV) complex in acidic medium should be mentioned. According to Beck [34], Ti(IV) stabilizes H_2O_2 (in 1:1.1 stoichiometry) in the form of the bidentately bound ligand and OO^{2-} to such an extent that this complex can be used as a stock titrimetric solution. On the other hand, Aubry [21] observed a 70% RTCO_2 yield in the presence of Ti(IV) and Zr(IV) in 0.1 mol dm^{-3} NaOH solutions.

It may also be considered that the rather active redox functions observed in the molybdate- (and the tungstate- and vanadate-) H_2O_2 systems may be assigned simply to metal ion catalysis involving changes in valence of the d_0 metal centres or to the formation of oxidizing radicals. These explanations, however, must be rejected because, in the presence of H_2O_2 in excess, neither lower oxidation state ions of these metals nor oxidizing radicals such as OH , HO_2 , H_2O_3 , etc. are to be expected.

Finally, we may refer to the widely known fact that H_2O_2 is a redox amphoteric substance: it is capable of both oxidation and reduction reactions: $\text{H}_2\text{O}_2 + 2\text{e} + 2\text{H}^+ \rightleftharpoons 2\text{H}_2\text{O}$ (1.77 V), and $\text{O}_2 + 2\text{e} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{O}_2$ (0.682 V). If these redox equilibria are added together, we obtain the electrode potential of $\text{O}_2 + 4\text{e} + 4\text{H}^+ \rightleftharpoons 2\text{H}_2\text{O}$, i.e. $\{1.226\text{ V}\} = (2 \times 1.77 + 2 \times 0.682/4)$ according to the Luther–Wilson rule [35a–c]. This mean of the two extreme redox potentials of H_2O_2 provides some orientation as to what reaction of H_2O_2 takes place with a given reactant. If the redox potential of the reagent is more positive than 1.226 V, then H_2O_2 will be oxidized to O_2 , whereas if it is more negative, then H_2O_2 will be reduced to H_2O . The redox potentials of certain d_0 metalates, i.e. molybdenum(VI), tungsten(VI) and vanadium(V), are all somewhat lower than 1.226 V, and consequently they are all incapable of the oxidation of H_2O_2 to O_2 , i.e. these oxidants cannot produce $^1\text{O}_2$ directly, albeit H_2O_2 is also in the singlet spin state.

4. Conclusions

It is generally accepted that, in neutral and alkaline solutions, the reaction of d_0 molybdate with H_2O_2 results in mono-, di-, tri- and tetraperoxo complexes. The reaction mixture behaves as a strong oxidizing agent because of the appearance of a hydroperoxo ligand in the predominant mixed ligand triperoxo

complex. At present, however, it cannot be decided whether triperoxomolybdate oxidizes the reductant directly or indirectly, because $^1\text{O}_2$ is detected in the absence of reductants, and the Mo(VI) triperoxo species alone has been found to be the only source

for this. In the presence of a phase-transfer reagent and in D₂O, the lifetime of ¹O₂ can be considerably lengthened.

Acknowledgements

My thanks are due to professor Tamás Kiss (Head of Department of Inorganic and Analytical Chemistry, University of Szeged, Szeged, Hungary) for ensuring working facilities after my retirement and for some financial support; to assistant professor Zoltán M. Galbács (Department of Inorganic and Analytical Chemistry, University of Szeged, Szeged, Hungary) for fruitful discussions and for his friendly contribution in collecting necessary information; to Dr. György Szöllösy research co-worker (Organic Catalysis Research Group, University of Szeged, Dóm tér 8., H-6720 Szeged, Hungary) and to Mr. Gábor Cseh chemistry student for their ready help in the on-line processing of the manuscript.

References

- [1] W. Muthmann, W. Nagel, *Berichte* 31 (1898) 1836.
- [2] J.B. Martinez, *Anales fis. y quim.* 40 (1944) 348.
- [3] (a) K.F. Jahr, *Berichte Ges. Freude T.H. Berlin* (1939) 91;
(b) K.F. Jahr, *Naturforsch. und Medizin in Deutschland 1939–1946 Fiat Review of German Science* 25 *Anorg. Chem. Teil III*, 170.
- [4] K. Gleu, *Z. Anorg. Allg. Chem.* 204 (1932) 67.
- [5] A. Rosenheim, M. Hakki, O. Krause, *Z. Anorg. Allg. Chem.* 209 (1932) 175.
- [6] N.J. Kobozev, N.N. Sokolow, *Z. Anorg. Allg. Chem.* 214 (1933) 321.
- [7] L.J. Csányi, *Acta Chim. Acad. Sci. Hung* 14 (1958) 69.
- [8] L.J. Csányi, *Transition Met. Chem.* 15 (1990) 371–373.
- [9] L.J. Csányi, I. Horvath, Z.M. Galbacs, *Transition Met. Chem.* 14 (1989) 90.
- [10] L.J. Csányi, *Acta Chim. Acad. Sci. Hung* 14 (1958) 79.
- [11] R.G. Beiles, R.A. Safina, E.M. Beiles, *Russ. J. Inorg. Chem.* 6 (1961) 825.
- [12] J.E. Huheey (Ed.), *Inorganic Chemistry*, third ed., Harper, Cambridge, 1983.
- [13] W.P. Griffith, *J. Chem. Soc.* (1963) 5345.
- [14] A. Mitschler, J.M. Le Carpentier, R.J. Weiss, *J. Chem. Soc., Chem. Commun.* (1968) 1260.
- [15] J.M. Le Carpentier, A. Mitschler, R. Weiss, *Acta Crystallogr.* B28 (1972) 1288.
- [16] (a) J.H. Campbell, A.C. Dengel, C.J. Edwards, W.P. Griffith, *J. Chem. Soc. Dalton Trans.* (1989) 1203;
(b) L.J. Csányi, *Acta Chim. Acad. Sci. Hung.* 14 (1958) 269.
- [17] J.M. Aubry, B. Cazin, *Inorg. Chem.* 27 (1988) 2013.
- [18] J.M. Aubry, B. Cazin, F. Duprat, *J. Org. Chem.* 54 (1989) 726.
- [19] K. Böhme, H.-D. Brauer, *Inorg. Chem.* 31 (1992) 3468.
- [20] Q.J. Niu, C.S. Foote, *Inorg. Chem.* 31 (1992) 3472.
- [21] J.M. Aubry, *J. Am. Chem. Soc.* 107 (1985) 5844.
- [22] J.D. Lydon, L.M. Schwane, R.C. Thompson, *Inorg. Chem.* 26 (1987) 2606.
- [23] L.M. Schwane, R.C. Thompson, *Inorg. Chem.* 28 (1989) 3938.
- [24] T.-J. Won, M. Balakrishna, R.C. Sudam, Thompson, *Inorg. Chem.* 33 (1994) 3804.
- [25] Th.R. Cundary, M.C. Zerner, R.S. Drago, *Inorg. Chem.* 27 (1988) 4239.
- [26] L.J. Csányi, K. Jáky, *J. Catal.* 127 (1991) 42.
- [27] (a) R.C. Thompson, in: G. Ondrejovič, A. Sirota (Eds.), *Contributions to Development of Coord. Chem.*, Slovak Techn. Univ. Press, Bratislava, 1993, pp. 315–318;
(b) R.C. Thompson, *Chem. Abstr.* 120 (1994) 254546j.
- [28] L.J. Csányi, *Kémiai Közlemények* 79 (1994) 51 (in Hungarian).
- [29] V. Nardello, J. Marko, G. Vermeersch, J.M. Aubry, *Inorg. Chem.* 34 (1995) 4950.
- [30] V. Nardello, S. Bouttemy, J.M. Aubry, *J. Mol. Catal. A: Chem.* 117 (1997) 439.
- [31] J.M. Aubry, S. Bouttemy, *J. Am. Chem. Soc.* 119 (1997) 5286.
- [32] V. Nardello, J. Marko, G. Vermeersch, J.M. Aubry, *Inorg. Chem.* 37 (1998) 5418.
- [33] J. Balej, *J. Electroanal. Chem.* 214 (1986) 481.
- [34] M.T. Beck, *Acta Chim. Acad. Sci. Hung.* 5 (1955) 209.
- [35] (a) R. Luther, D.R. Wilson, *Z. Phys. Chem.* 34 (1900) 488;
(b) R. Luther, D.R. Wilson, *Z. Phys. Chem.* 36 (1902) 385;
(c) L.J. Csányi, *J. Chem. Educ.* 37 (1960) 147.