# Reactivity of $HO_2/O_2^-$ Radicals in Aqueous Solution

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Kinetic data for the superoxide radical ($HO_2 \rightleftharpoons O_2^- + H^+$, $pK = 4.8$) in aqueous solution have been critically assessed. Rate constants for reactions of $O_2^-$ and $HO_2$ with more than 300 organic and inorganic ions, molecules and other transient species have been tabulated.

Key words: aqueous solution; chemical kinetics; data compilation; perhydroxyl radical; rate constants; review; superoxide radical.

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## 1. Introduction

The past decade has seen a renewed interest in the possible role the superoxide/perhydroxyl ($O_2^-/HO_2$) radicals play in biological systems, in radiation and UV-photolysis induced oxidations in the presence of oxygen, in the autoxidation of industrially important chemicals, in the oxidation of numerous compounds in the atmosphere, etc. This, in turn, has resulted in a substantial increase in the number of studies describing the reactions between $HO_2/O_2^-$ radicals and specific compounds in an effort to unravel the kinetics and mechanisms of some of these systems [1–7].[a)]

In this introduction a brief discussion of the generation of $HO_2/O_2^-$ radicals in aqueous solutions, the spectral characteristics and detection of these radicals and their kinetic properties will be presented. Finally, the acid-base dependent kinetic equations necessary for the description of $HO_2/O_2^-$ reactions will be developed in detail as these kinetics are not well known. Although the kinetic



[a)] Figures in brackets indicate literature references at the end of the text.

descriptions are applicable to many systems, they do not consider a number of important complications, i.e. those systems in which reactions of product transients with oxygen or hydrogen peroxide occur, possible chain reactions, etc.

*It should be noted that this entire review is applicable to aqueous solutions or systems that retain aqueous characteristics only.*

## 2. Generation of $HO_2/O_2^-$ in Aqueous Solutions

While there are numerous reactions in which $HO_2/O_2^-$ can be generated in aqueous solutions, only the three most commonly used methods involving radiolysis, photolysis and the xanthine oxidase system will be discussed here. Because of the similarity of the mechanisms, the generation of $HO_2/O_2^-$ by radiolysis and photolysis will be discussed together.

### 2.1. Radiolytic and Photolytic Generation of $HO_2/O_2^-$

The initial energy deposition processes and hence the primary radical distribution are different for high energy ionizing radiation, Eq. (I), and VUV-photolysis, Eq. (II):

$$H_2O \text{—}\wwwarrow \text{H, } e_{aq}^-, \text{ OH, } H_2, H_2O_2, H_3O^+ \qquad \text{(I)}$$

$$H_2O \xrightarrow{h\nu} \text{H, OH} \qquad \text{(II)}$$

However extensive studies have shown that the subsequent reactions by which the primary radicals H, $e_{aq}^-$ and OH are converted to $HO_2/O_2^-$ in the presence of formate are similar:

$$e_{aq}^- + O_2 \rightarrow O_2^- \qquad (1)$$
$$k_1 = 2.0 \times 10^{10} \text{ L mol}^{-1}\text{s}^{-1} \text{ [8a]}$$

$$e_{aq}^- + H^+ \rightarrow H \qquad (2)$$
$$k_2 = 2.2 \times 10^{10} \text{ L mol}^{-1}\text{s}^{-1} \text{ [8a,b]}$$

$$H + O_2 \rightarrow HO_2 \qquad (3)$$
$$k_3 = 2 \times 10^{10} \text{ L mol}^{-1}\text{s}^{-1} \text{ [9]}$$

$$HCO_2^- + OH \rightarrow CO_2^- + H_2O \qquad (4)$$
$$k_4 = 3.5 \times 10^{9} \text{ L mol}^{-1}\text{s}^{-1} \text{ [10]}$$

$$HCO_2^- + H \rightarrow CO_2^- + H_2 \qquad (5)$$
$$k_5 = 1.3 \times 10^{8} \text{ L mol}^{-1}\text{s}^{-1} \text{ [11]}$$

$$CO_2^- + O_2 \rightarrow CO_2 + O_2^- \qquad (6)$$
$$k_6 = 2.4 \times 10^{9} \text{ L mol}^{-1}\text{s}^{-1} \text{ [12]}$$

where the $O_2^-$ radical is always in equilibrium with its conjugate acid, the perhydroxyl radical

$$HO_2 \rightleftharpoons H^+ + O_2^- \qquad (7,-7)$$

$$K_{HO_2} = 1.6 \times 10^{-5} \text{ mol L}^{-1} \text{ (see Sec. 5)}$$

The formate system is particularily useful since the quantitative conversion of the primary radicals to $HO_2/O_2^-$, which occurs at near diffusion controlled rates, is independent of pH. Detailed methods for the preparation of aqueous $HO_2/O_2^-$ solutions have been published [13,14].

Some alcohols (ethanol, methanol, 2-propanol) can be substituted for formate.

$$CH_3CH_2OH + OH \rightarrow CH_3\dot{C}HOH + H_2O \qquad (8)$$

$$CH_3CH_2OH + OH \rightarrow CH_3CH_2O\cdot + H_2O \qquad (9)$$

$$CH_3CH_2O\cdot + CH_3CH_2OH \rightarrow CH_3CH_2OH + CH_3\dot{C}HOH \qquad (10)$$

$$CH_3CH_2OH + H \rightarrow CH_3\dot{C}HOH + H_2 \qquad (11)$$

$$CH_3\dot{C}HOH + O_2 \rightarrow CH_3CH(\dot{O}_2)OH \qquad (12)$$

$$CH_3CH(\dot{O}_2)OH + OH^- \rightarrow CH_3CHO + H_2O + O_2^- \qquad (13)$$

The quantity of alcohol must be sufficiently small such that the solution retains its aqueous characteristics. It should be noted that aqueous alcoholic systems are efficient only in the alkaline range since reaction (13) is base catalyzed. The preparation of such solutions has been described elsewhere [14–16].

One of the oldest methods for generating $HO_2/O_2^-$ involves the radiolysis/photolysis of aqueous hydrogen peroxide solutions [17]. Here, after the initial primary radical formation, Eqs. (I) and (II), both $e_{aq}^-$ and H are converted to OH radicals by reaction with peroxide,

$$e_{aq}^- + H_2O_2 \rightarrow OH + OH^- \qquad (14)$$

$$H + H_2O_2 \rightarrow OH + H_2O \qquad (15)$$

while the photolysis of peroxide yields OH radicals directly,

$$H_2O_2 \rightarrow 2\ OH. \qquad (16)$$

The OH radicals then react with hydrogen peroxide to yield $HO_2$,

$$OH + H_2O_2 \rightarrow HO_2 + H_2O. \qquad (17)$$

As has been shown earlier, in this system $HO_2/O_2^-$ can be generated anaerobically as well as aerobically [18].

### 2.2. Enzymatic Generation of $O_2^-$

Researchers in the biomedical fields preferentially use enzymatic methods for the generation of superoxide radicals as they are closest to *in vivo* situations. The most-frequently used enzyme for this purpose is xanthine oxidase [19,20]. The overall process is given by reactions (18) and (19):

$$\text{Enzyme-H}_2 + 2\ O_2 \rightarrow \text{Enzyme} + 2\ H^+ + 2\ O_2^- \quad (18)$$

$$\text{Enzyme-H}_2 + O_2 \rightarrow \text{Enzyme} + H_2O_2 \quad (19)$$

Preferred substrates for this enzyme are either xanthine or acetaldehyde which are oxidized to uric acid and acetic acid respectively while the enzyme is reduced by accepting two electrons. In the presence of molecular oxygen the reduced enzyme can lose these electrons by two different pathways, a univalent reaction step leading to $O_2^-$ formation (reaction 18) and a divalent reaction step (reaction 19) leading to direct formation of hydrogen peroxide. The predominance of one reaction over the other is controlled by the pH of the medium, the oxygen concentration and the turnover rate of the enzyme. Although this method has been used successfully in competition kinetics, it is limited to the pH range in which xanthine oxidase is active.

There appears to be a general consensus that the successful use of any of the superoxide generating methods depends strongly upon the absence of catalytic impurities in the system. The presence of certain metallic impurities is known not only to accelerate the spontaneous disproportionation of the $HO_2/O_2^-$ radicals (see Sec. 5) thus causing a rapid build-up of hydrogen peroxide, but also to initiate Fenton-type reactions ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH + OH^-$ [21]) that could obscure the reaction(s) under study.

## 3. Spectral Characteristics of $HO_2/O_2^-$

Both $HO_2$ and $O_2^-$ have distinct absorption spectra in the low UV region with maxima at 225 and 245 nm respectively, Fig. 1. The molar extinction coefficients used in this review were determined by the stopped-flow radiolysis technique [21a] and are based on the molar extinction coefficients of nitroform ($\epsilon^{350nm} = 14{,}800 \pm 200$ L mol$^{-1}$cm$^{-1}$, [22–24]) and cytochrome C ($\Delta\epsilon^{550nm}$ [Fe(II) cyt C - Fe(III )cyt C] = 21,100 L mol$^{-1}$cm$^{-1}$ [25]) without assuming $G$ values [26]. At pH 1.5 $\epsilon_{HO_2}^{225nm} = 1400 \pm 80$ L mol$^{-1}$cm$^{-1}$; at pH 10.5 $\epsilon_{O_2^-}^{245nm} = 2350 \pm 120$ L mol$^{-1}$cm$^{-1}$. As $HO_2$ and $O_2^-$ are in equilibrium (7, −7) the effective molar extinction coefficient varies with pH; see Table 1a.

$$\epsilon_{\text{effective}} = \left[\frac{[HO_2]}{[HO_2] + [O_2^-]}\right]\epsilon_{HO_2} + \left[\frac{[O_2^-]}{[O_2^-] + [HO_2]}\right]\epsilon_{O_2} \quad \text{(III)}$$

It should be noted that these effective extinction coefficients refer to the total radical concentration prior to spontaneous disproportionation and thus prior to peroxide formation. Any extinction coefficients must be corrected for the absorption of $H_2O_2$ (from reactions 23 and 24) if they are to be used for computation of decay rates. Since, as indicated in reactions (23) and (24), a mole of $HO_2$ or $O_2^-$ produces a half mole of $H_2O_2$, the effective extinction coefficient has to be corrected for the absorbance of the latter:

$$\epsilon_{\text{effective (corrected)}} = (\epsilon_{HO_2/O_2^-} - 0.5\ \epsilon_{H_2O_2}) \quad \text{(IV)}$$

These corrected extinction coefficients are found in Table 1b; it should be noted that the correction is most significant at low wavelengths and high pH.

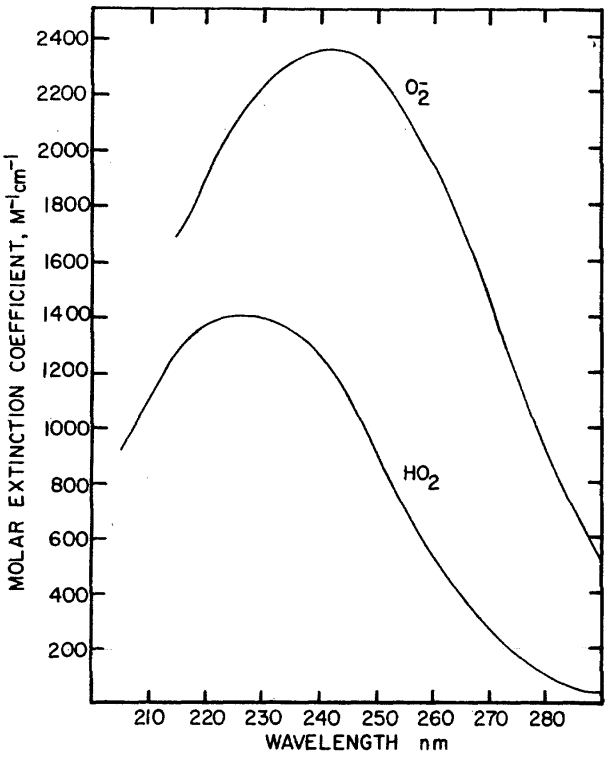


FIG. 1. Absorption spectra of $HO_2$ in air-saturated $HClO_4$ solution at pH 1.5 and $O_2^-$ in air-saturated 0.01 mol L$^{-1}$ sodium formate solution containing $1 \times 10^{-4}$ mol L$^{-1}$ EDTA at pH 10.5 [26].

TABLE 1a. Effective extinction coefficient ($\epsilon_{\text{effective}}^{\lambda}$, L mol$^{-1}$ cm$^{-1}$) of the total radical concentration [R·] = [$HO_2$] + [$O_2^-$] for selected wavelength and pH values calculated by equation (III) at 23 °C

| pH | $\epsilon^{230nm}$ | $\epsilon^{240nm}$ | $\epsilon^{250nm}$ | $\epsilon^{260nm}$ |
|---|---|---|---|---|
| 0.5–1.5 | 1400 | 1260 | 915 | 540 |
| 2.0 | 1401 | 1261 | 917 | 542 |
| 2.5 | 1404 | 1265 | 922 | 547 |
| 3.0 | 1413 | 1277 | 936 | 562 |
| 3.5 | 1440 | 1312 | 979 | 699 |
| 4.0 | 1514 | 1410 | 1101 | 733 |
| 4.5 | 1679 | 1624 | 1366 | 1010 |
| 5.0 | 1911 | 1928 | 1745 | 1402 |
| 5.5 | 2093 | 2166 | 2038 | 1709 |
| 6.0 | 2181 | 2281 | 2181 | 1858 |
| 6.5 | 2214 | 2324 | 2234 | 1913 |
| 7.0 | 2225 | 2338 | 2252 | 1931 |
| 7.5 | 2228 | 2343 | 2257 | 1937 |
| 8.0–13.0 | 2230 | 2345 | 2260 | 1940 |

TABLE 1b. Effective extinction coefficient ($\epsilon^{\lambda}_{\text{effective(corrected)}}$, L mol$^{-1}$ cm$^{-1}$) of the total radical concentration [R·] = [$HO_2$] + [$O_2^-$] corrected for the absorption of $H_2O_2$ formed during decay, $\epsilon_{\text{for decay}} = (\epsilon_{R\cdot} - 0.5\,\epsilon_{H_2O_2})$ at 23 °C[a]

| pH | $\epsilon^{230nm}$ | $\epsilon^{240nm}$ | $\epsilon^{250nm}$ | $\epsilon^{260nm}$ |
|---|---|---|---|---|
| 0.5–1.5 | 1368 | 1241 | 904 | 534 |
| 2.0 | 1369 | 1242 | 906 | 536 |
| 2.5 | 1372 | 1246 | 911 | 541 |
| 3.0 | 1381 | 1248 | 925 | 556 |
| 3.5 | 1408 | 1293 | 968 | 693 |
| 4.0 | 1482 | 1391 | 1090 | 727 |
| 4.5 | 1647 | 1423 | 1355 | 1004 |
| 5.0 | 1879 | 1909 | 1734 | 1396 |
| 5.5 | 2061 | 2147 | 1949 | 1703 |
| 6.0 | 2149 | 2262 | 2170 | 1852 |
| 6.5 | 2182 | 2305 | 2223 | 1907 |
| 7.0 | 2193 | 2319 | 2241 | 1925 |
| 7.5 | 2196 | 2324 | 2246 | 1931 |
| 8.0–9.0 | 2198 | 2326 | 2248 | 1933 |
| 9.5 | 2195 | 2324 | 2248 | 1932 |
| 10.0 | 2188 | 2319 | 2244 | 1929 |
| 10.5 | 2175 | 2307 | 2235 | 1923 |
| 11.0 | 2150 | 2287 | 2219 | 1913 |
| 11.5 | 2100 | 2245 | 2188 | 1893 |
| 12.0 | 2053 | 2205 | 2156 | 1869 |
| 12.5 | 2025 | 2183 | 2139 | 1856 |
| 13.0 | 2015 | 2173 | 2134 | 1850 |

[a] See [30] for the absorption spectrum of $H_2O_2$.

## 4. Detection of $HO_2/O_2^-$ Radicals

A wide variety of methods has been used in the detection of $HO_2/O_2^-$ radicals. The most direct of these is the optical detection of the low UV absorbances discussed in Sec. 3. In addition both $HO_2$ and $O_2^-$ have characteristic electron spin resonance spectra with the former detectable at ambient temperatures in acidic solutions [27] while the latter can be detected only in ices at very low temperatures [28]. As a corollary to the esr technique, spin traps have also been used [29].

The most widely used method of detecting superoxide radicals is through the use of such chemical indicators as tetranitromethane, Nitro Blue Tetrazolium and cytochrome C which form products with intense optical absorbance:

$$C(NO_2)_4 + O_2^- \rightarrow C(NO_2)_3^- + NO_2 + O_2 \qquad (20)$$

$$\text{Cyt C } (Fe^{3+}) + O_2^- \rightarrow \text{Cyt C } (Fe^{2+}) + O_2 \qquad (21)$$

$$NBT^{2+} + O_2^- \rightarrow 1/2\ MF^+ + O_2 \qquad (22)$$

The respective rate constants for reactions (20) to (22) are given in Table 3. All of these indicators are most advantageously used at pH near neutrality. Such indicators have been used competitively to determine relative reaction rates for other solutes with $HO_2/O_2^-$. Some of the compounds react by complicated mechanisms and should not be used in competition kinetics without consulting the original articles cited in Table 3.

## 5. Kinetics of Disproportionation of $HO_2/O_2^-$

Both $HO_2$ and $O_2^-$ have been shown to disappear by second-order processes that vary with pH in aqueous solutions. Since $HO_2$ is always in equilibrium with $O_2^-$, reaction (7,–7), the spontaneous disproportionation can be described by the following reactions:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (23)$$

$$HO_2 + O_2^- + H_2O \rightarrow H_2O_2 + O_2 + OH^- \qquad (24)$$

An equation can be derived that gives the experimentally observed rates ($k_{obs}$) in terms of the rate constants for reactions (23) and (24) and the equilibrium constant $K_{HO_2}$:

$$k_{obs} = \frac{k_{23} + k_{24}(K_{HO_2}/[H^+])}{(1 + K_{HO_2}/[H^+])^2} \qquad (V)$$

A value for $K_{HO_2}$ can be obtained independently from spectrophotometric measurements as well as from Eq. (V). As $k_{obs}$ is invariant to pH in the range of 0.0 to 1.5, a value for $k_{23}$ can be measured directly (i.e. $k_{obs} = k_{23}$ at pH 1.5). The rate constant $k_{24}$, however, must be calculated from Eq. (V), using $k_{23}$ and $K_{HO_2}$. The results from a number of studies of the spontaneous disproportionation of $HO_2/O_2^-$, where the experimentally determined rates were all normalized by the molar extinction coefficients reported previously [26], yield the best average values of $k_{23} = (8.3 \pm 0.7) \times 10^5$ L mol$^{-1}$s$^{-1}$ [26,30–33], $k_{24} = (9.7 \pm 0.6) \times 10^7$ L mol$^{-1}$s$^{-1}$ [26,30,31,33] and $K_{HO_2} = 1.6 \times 10^{-5}$ mol L$^{-1}$ [26,30,31,33–35,53] or $pK_a(HO_2) = 4.8 \pm 0.1$. Although other studies have shown that $pK_a$ can vary with ionic strength [36], $pK_a(HO_2)$ was found to be invariant within experimental error over a formate concentration of $10^{-3}$–$10^{-1}$ mol L$^{-1}$. The curve shown in Figure 2 was calculated from these values and Eq. (V) and was found to be in very good agreement with the experimental data from a number of laboratories [30–33,37,38]

Two important features of Figure 2 should be noted. First, it is apparent that the curve has a slope of $-1$ above pH 6. At high pH, Eq. (V) reduces to

$$k_{obs} = k_{24}[H^+]/K_{HO_2} = 6 \times 10^{12}[H^+],\ \text{L mol}^{-1}\text{s}^{-1} \qquad (VI)$$

giving a convenient method for calculating the spontaneous rate of disproportionation at a specific pH (pH > 6). Secondly, since the lowest reported $k_{obs} = 0.3$ L mol$^{-1}$s$^{-1}$ at pH 13 is still on the straight line and hence represents reaction (24), one can conclude that the rate for a reaction between two $O_2^-$ radicals (e.g. $O_2^- + O_2^-$) in aqueous solutions is for all practical purposes negligible.

The kinetic and spectral data for $HO_2$ and $O_2^-$ discussed above are listed in Table 2 along with other properties for the radicals in aqueous solution.

## 6. Reactions of $HO_2/O_2^-$ with Substrates

### 6.1. Kinetics

As mentioned previously, $HO_2$ is in a pH-dependent equilibrium with $O_2^-$. Further, many substrates can themselves ionize (equilibria (25,–25) and (26,–26)). Such

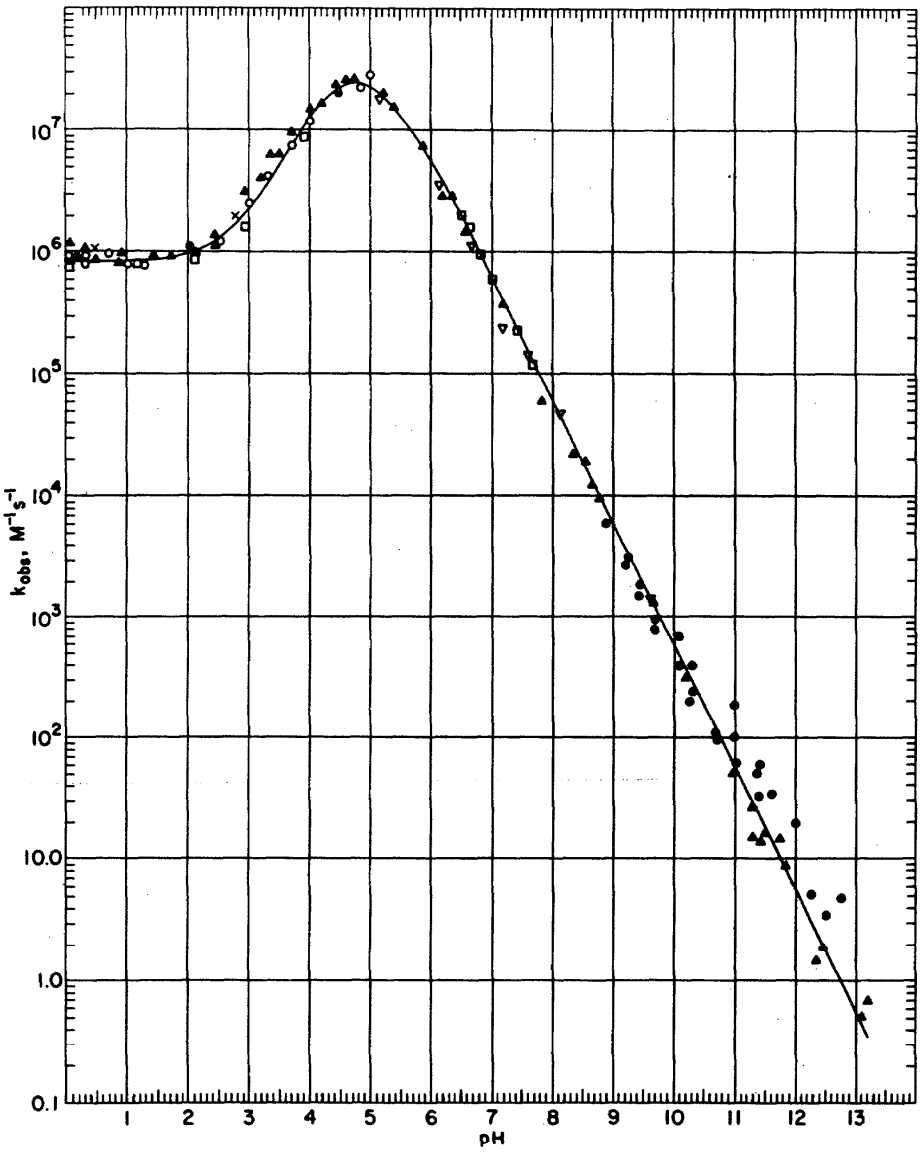


FIG. 2. Observed second-order rate constant, $k_{obs}$ in Eq. (V), for the decay of $HO_2/O_2^-$ plotted as a function of pH: ▲ Bielski and Allen [30], ●Marklund [37], × Sehested, et al. [38], O Bielski and Schwarz [32], □ Behar, et al. [31], ▽ Rabani and Nielsen [33].

dissociations not only influence the thermodynamics of the system but also the kinetics of reactions may be dramatically altered by protonation or dissociation. Hence, great care should be taken in extrapolating rate data reported at one pH in Table 3 to solutions of different pH. Ionization equilibria in substrates, including ionization of radical intermediates, are thus highly relevant to the chemistry of $HO_2/O_2^-$ in aqueous media. A detailed kinetic treatment of such systems is given below, although it should be stressed that in many instances experimental conditions can be adjusted such that only one or two equilibria need be considered and the required kinetic treatment is then much simplified. A complete description of the interaction between $HO_2/O_2^-$ and a species ($QH_2$) and its dissociation products ($QH^-$,$Q^{2-}$), with the assumption that the initial reaction produces a free radical that can in turn react with $HO_2/O_2^-$ or disproportionate, involves four equilibria and thirteen reactions:

Equilibria: $HO_2 \rightleftharpoons O_2^- + H^+$, $pK_1 = 4.8$ (7,−7)

$QH_2 \rightleftharpoons QH^- + H^+$, $pK_2$ (25,−25)

$QH^- \rightleftharpoons Q^{2-} + H^+$, $pK_3$ (26,−26)

$QH\cdot \rightleftharpoons Q\cdot^- + H^+$, $pK_4$ (27,−27)

Reactions: $QH_2 + HO_2 \rightarrow QH\cdot + H_2O_2$ (28)

TABLE 2. Properties of $HO_2/O_2^-$ in aqueous solution

| Property | $HO_2$(aq) | $O_2^-$(aq) |
|---|---|---|
| Reduction potential[a] ($O_2 + e^- \rightarrow O_2^-$), pH 7 | | −0.33 V [45,54,55] |
| $pK_a$ | 4.8 [26,30,31,33,35,53] | |
| Diffusion constant ($cm^2\ s^{-1}$) | | $1.5 \times 10^{-5}$ [b] [48] |
| $\Delta H_f°$(298 K) (kcal $mol^{-1}$) | −8.6 ± 1 [47] | −5.9 ± 1 [47]<br>−8 ± 2 [46] |
| $S°$(298 K) (cal $mol^{-1}\ K^{-1}$) | 33 ± 1 [47] | 19 [47] |
| Enthalpy of hydration (kcal $mol^{-1}$) | | −94 [46]<br>−95 [47] |
| Free energy of hydration (kcal $mol^{-1}$) | | −85 [49] |
| Entropy of hydration (cal $K^{-1}\ mol^{-1}$) | −22 [49] | −29.6 [49] |
| Enthalpy of ionization (kcal $mol^{-1}$) | 0 [46]<br>2.7 ± 0.7 [18]<br>1.0 [49] | |
| Entropy of ionization (cal $K^{-1}\ mol^{-1}$) | −17.4 [49] | |
| Electron affinity (eV) | 1.85 ± 0.12[c] [47] | |
| $\lambda_{max}$ (nm) | 225 [26] | 245 [26] |
| $\epsilon_{max}$(L $mol^{-1}\ cm^{-1}$) | 1400 ± 80 [26] | 2350 ± 120 [26] |
| $k(HO_2 + HO_2) = (8.3 \pm 0.7) \times 10^5$ (L $mol^{-1}\ s^{-1}$) (See Sec. 5) | | |
| $k(HO_2 + O_2^-) = (9.7 \pm 0.6) \times 10^7$ (L $mol^{-1}\ s^{-1}$) (See Sec. 5) | | |
| $E_a(HO_2 + HO_2) = 4.9$–$5.9$ (kcal $mol^{-1}$) [32,46] | | |
| $E_a(HO_2 + O_2^-) = 2.1$ (kcal $mol^{-1}$) [32] | | |

[a] Standard state: 1 atm $O_2$.
[b] Soln. contg. 0.1 mol $L^{-1}$ NaOH, 10 vol % PrOH.
[c] Gas phase.

$$QH_2 + O_2^- \rightarrow QH\cdot + HO_2^- \quad (29)$$

$$QH^- + HO_2 \rightarrow QH\cdot + HO_2^- \quad (30)$$

$$QH^- + O_2^- \rightarrow Q\cdot^- + HO_2^- \quad (31)$$

$$Q^{2-} + HO_2 \rightarrow Q\cdot^- + HO_2^- \quad (32)$$

$$Q^{2-} + O_2^- \rightarrow \text{(transient or product)} \quad (33)$$

$$QH\cdot + HO_2 \rightarrow Q + H_2O_2 \quad (34)$$

$$QH\cdot + O_2^- \rightarrow Q + HO_2^- \quad (35)$$

$$Q\cdot^- + HO_2 \rightarrow Q + HO_2^- \quad (36)$$

$$Q\cdot^- + O_2^- \rightarrow \text{(transient or product)} \quad (37)$$

$$QH\cdot + QH\cdot \rightarrow Q + QH_2 \quad (38)$$

$$QH\cdot + Q\cdot^- \rightarrow Q + QH^- \quad (39)$$

$$Q\cdot^- + Q\cdot^- \rightarrow Q + Q^{2-} \quad (40)$$

If all acid-base equilibria are ignored, this system reduces in principle to three second-order reactions that are in parallel and, in part, in series:

$$A + B \rightarrow C \quad (41)$$

$$B + C \rightarrow D \quad (42)$$

$$C + C \rightarrow D + A \quad (43)$$

Such a system has no simple solution; solutions for a mechanism involving only reactions (41) and (42) have been described in detail elsewhere [39–41] and are not trivial. However, experimental conditions can usually be adjusted such that two of the three reactions drop out, thus allowing for simple kinetic solutions. In the following kinetic development, reactions (41) through (43) will be discussed as independent systems and rate equations will be derived for the individual reactions in terms of their pH dependence.

A complete description of the initial step in the mechanism involves the equilibria (7,−7), (25,−25) and (26,−26) and reactions (28) to (33). The rate of disappearance of the radical ([R] = [$HO_2$] + [$O_2^-$]) is given by:

$$-\frac{d[R]}{dt} = k_{28}[QH_2][HO_2] + k_{29}[QH_2][O_2^-] + k_{30}[QH^-][HO_2] + k_{31}[QH^-][O_2^-] + k_{32}[Q^{2-}][HO_2] + k_{33}[Q^{2-}][O_2^-] \quad (VII)$$

Rearrangement of the equilibria (7,−7), (25,−25) and (26,−26) leads to the following relationships:

$$[O_2^-] = [HO_2](K_{HO_2}/[H^+]) = [HO_2]Y_1$$

$$[QH^-] = [QH_2](K_{25}/[H^+]) = [QH_2]Y_2$$

$$[Q^{2-}] = [QH_2](K_{25}K_{26}/[H^+]^2) = [QH_2]Y_2Y_3$$

Substituting these relationships into Eq. (VII) leads to:

$$-\frac{d[R]}{dt} = [HO_2][QH_2](k_{28} + k_{29}Y_1 + k_{30}Y_2 + k_{31}Y_1Y_2 + k_{32}Y_2Y_3 + k_{33}Y_1Y_2Y_3) \quad (VIII)$$

The total concentration of species S is given by [S] = [$QH_2$] + [$QH^-$] + [$Q^{2-}$] or [S] = [$QH_2$](1 + $Y_2$ + $Y_2Y_3$) and the total $HO_2/O_2^-$ concentration is given by [R] = [$HO_2$](1 + $Y_1$). Substituting these relationships into Eq. (VIII) gives:

$$-\frac{d[R]}{dt} = \frac{[R][S](k_{28} + k_{29}Y_1 + k_{30}Y_2 + k_{31}Y_1Y_2 + k_{32}Y_2Y_3 + k_{33}Y_1Y_2Y_3)}{(1 + Y_1)(1 + Y_2 + Y_2Y_3)} \quad (IX)$$

Under first-order conditions where [S] is approximately constant, that is [S]≫[R], Eq. (IX) can be integrated to yield:

$$k = \frac{[S](k_{28} + k_{29}Y_1 + k_{30}Y_2 + k_{31}Y_1Y_2 + k_{32}Y_2Y_3 + k_{33}Y_1Y_2Y_3)}{(1 + Y_1)(1 + Y_2 + Y_2Y_3)} \quad (X)$$

where $k_{obs} = k/[S]$. Equation (X) describes the pH dependent kinetics of the reactions between $HO_2/O_2^-$ and a compound with two p$K$'s. This equation is simplified for compounds with one or no p$K$ in the pH range studied. An example of this case can be found in the reaction between $HO_2/O_2^-$ and tetranitromethane [23].

The model system becomes more complex if the reaction between $QH_2$ and $HO_2/O_2^-$ produces a transient with an acid-base equilibrium (27,−27) that can also react with $HO_2/O_2^-$ (reactions (34) to (37)). Following an analogous procedure to that used for the derivation of Eq. (V) and using the relationship

$$[Q\cdot^-] = [QH\cdot](K_{27}/[H^+]) = [QH\cdot]Y_4$$

one obtains (defining [S·] = [QH·] + [$Q\cdot^-$]):

$$-\frac{d[R]}{dt} = \frac{[R][S\cdot](k_{34} + k_{35}Y_1 + k_{36}Y_4 + k_{37}Y_1Y_4)}{(1 + Y_1)(1 + Y_4)} \quad (XI)$$

Detailed solutions for equations of this general form, where [R] ≠ [S·], are complex and will not be discussed here. Since radical-radical reactions of this nature generally occur on a very fast time scale, they can be measured only by fast kinetic techniques (flash photolysis or pulse radiolysis) where, with proper experimental design, equal amounts of [R] and [S·] are produced. Under these conditions Eq. (XI) can be integrated to yield:

$$k_{obs} = \frac{(k_{34} + k_{35}Y_1 + k_{36}Y_4 + k_{37}Y_1Y_4)}{(1 + Y_1)(1 + Y_4)} \quad (XII)$$

This equation describes a second-order reaction between two radicals, both having p$K$s, in which the radicals are generated independently and not from reactions (28) to (33). In fact, under the experimental conditions being considered, S· is generated from the reactions between $HO_2/O_2^-$ and S (as in the generalized reactions (41) and (42)). If the rate of the $HO_2/O_2^-$-radical reaction (42) is much slower than the rate at which the radical is generated (41), then reaction (42) will never occur since all of the $HO_2$ is consumed in reaction (41). On the other hand, if the rate of reaction (42) is much faster than reaction (41) steady state conditions prevail and the overall reaction becomes A + 2B → D. Therefore, the observed rate is now twice the true rate of reaction (41). This concept is introduced into Eq. (X) and (XII) by calculating the observed rates of reaction at a particular pH to determine which rate is faster at those specific experimental conditions and hence whether a factor of two must be included in Eq. (X). Such a situation has been described in the ascorbic acid system [42,43].

The final reaction in the model system involves the disproportionation of S· as described by reactions (38) and (40). The rates of disappearance of the radicals [QH·] and [$Q\cdot^-$] are given by:

$$-\frac{d[QH\cdot]}{dt} = 2k_{38}[QH\cdot]^2 + k_{39}[QH\cdot][Q\cdot^-] \quad \text{(XIII)}$$

$$-\frac{d[Q\cdot^-]}{dt} = k_{39}[QH\cdot][Q\cdot^-] + 2k_{40}[Q\cdot^-]^2 \quad \text{(XIV)}$$

and, substituting the relationship derived from equilibrium (27,−27), the rate of disappearance of the total radical concentration is given by the sum of Eqs. (XIII) and (XIV)

$$-\frac{d([QH\cdot] + [Q\cdot^-])}{dt} = \frac{2[S\cdot]^2(k_{38} + k_{39}Y_4 + k_{40}Y_4)^2}{(1 + Y_4)^2} \quad \text{(XV)}$$

and the observed second-order rate of disproportionation is merely

$$k_{obs} = \frac{2(k_{38} + k_{39}Y_4 + k_{40}Y_4)^2}{(1 + Y_4)^2} \quad \text{(XVI)}$$

The kinetics described by Eq. (XVI) gives the rate at which reaction (43) occurs as a function of pH when the radical S· has a p$K$. If reaction (43) occurs at a faster rate than reaction (42) then the system reduces to the formation of a transient which subsequently disappears by reaction with itself. In a system of this nature Eqs. (X) and (XVI) can be used independently to describe the kinetics of the entire system. As is apparent the kinetics that describe the spontaneous disproportionation of $HO_2/O_2^-$, Eq. (V), are merely a reduced form of Eq. (XVI) omitting the reaction of $(O_2^- + O_2^-)$ which is negligible as described in section 5.

### 6.2. Criteria for Assessment of the Kinetic Data

All of the data reported in Table 3 fall into two categories: (1) rate constants and (2) observed specific rates of reactions. An observed specific rate, $k(HO_2/O_2^- + X)$, is taken to represent a value valid under the specific experimental conditions reported by the authors whereas a rate constant, $k(HO_2 + X)$ or $k(O_2^- + X)$, is considered to be independent of pH (but not of temperature, ionic strength, etc.) and to represent the rate at which either $HO_2$ or $O_2^-$ reacts with a given compound. A value of $k_{obs}$ at a specific pH can be calculated by equation (X) if the rate constants for the reaction of $HO_2$ and $O_2^-$ with that particular compound are known.

The following criteria were considered with regard to all of the rate studies listed in this table:

1. Whether, when pseudo first-order conditions were used, the rates were determined over a broad concentration range and corrected, if necessary, for the spontaneous disproportionation of $HO_2/O_2^-$.

2. Whether the reaction was studied either as a function of pH or under conditions such that only one of the two species reacted. Thus, $k_{obs} = 10^8$ L mol$^{-1}$ s$^{-1}$ at pH 8 must be for $k(O_2^- + X)$ and not $k(HO_2 + X)$, using equation (X), a limiting value for $k(HO_2 + X)$ of $10^{10}$ L mol$^{-1}$ s$^{-1}$ and assuming that the scavenger has no p$K$ in this pH region.

3. Whether the reaction rate was found to be anomalous with respect to other studies of that particular reaction.

Comments relating to the above criteria are included in some entries in the table. In some studies it was impossible to ascertain details concerning either the experimental conditions or the kinetic analysis; such studies were nevertheless included in the table if they contained the only reported rates for these reactions.

Comments are also included when there are unexplained discrepancies in the data; the discrepancies may be due to differing experimental conditions or other reasons. It is hoped that further studies of some of these reactions will be carried out to resolve the conflicting data.

### 6.3. Explanation of Table 3

Table 3 contains rate constants for reactions of $HO_2/O_2^-$ with various inorganic and organic solutes and other radical species in aqueous solution. The inorganic reactants are listed first, alphabetized by main element. Within the groupings by element the arrangement is in order of increasing oxidation state. Within a particular oxidation state for a metal, aquated ions are listed first followed by complexes with neutral ligands (amines), amino acids and other organic acids; polynuclear metal species are listed last. The metal ions are generally shown without ligated $H_2O$ (and $OH^-$ at high pH). The inorganic reactants are followed by the organic reactants, arranged alphabetically by name. Common names have been used in many cases and both a compound name index containing synonyms and a molecular formula index are provided as an aid to locating particular reactants.

The table entry number is followed by the name for the reactant. Reactions include products only when evidence for their identity has been reported. The radical has been given as either $HO_2$ or $O_2^-$ when conditions were such that one species would predominate or when the study was carried out over a broad pH range with kinetic analysis as described above. Where studies were under conditions insufficient to determine the individual rate constants, the radical has been given as $HO_2/O_2^-$ and the observed specific rate should be understood to be for an unspecified mixture of the two radical species. When the studies were carried out near the p$K$ of a reactant and the contributions of the individual species were not determined, the p$K$ [51] has been included in the table entry and the rate constant should be understood to be for a mixture of reactant species.

When the rate constants were corrected by the original authors for ionic strength it has been noted (cor. for $I$). The reviewers did not attempt to make such corrections because of uncertainties such as actual charge on the ions, concentrations, etc.

In some cases the reactant serves as a catalyst for the disproportionation of $HO_2/O_2^-$; for example, superoxide dismutase (SOD) and a number of copper complexes catalyze the formation of hydrogen peroxide and oxygen by a mechanism involving successive reduction and oxidation of the metal center [51,52]. Rate constants which are for the overall catalyzed reaction,

$$2\,O_2^- + 2\,H_2O \xrightarrow{\text{cat.}} H_2O_2 + O_2 + 2\,OH^-,$$

have been determined for various metal-centered species. Whenever the rate constants listed herein are for $k_{\text{catalytic}}$ the reaction is written accordingly or that information is given as a notation in the *Comments* column.

Error limits assigned by authors of the original papers have been included with the rate constants in column 3. Upper limits for rate constants for systems in which no reaction was observed have been included whenever they could be derived from the experimental conditions. Otherwise, the statement that no reaction was observed is included as a comment and the original paper should be consulted. In some cases the rate constants were calculated with reference to the rate constant for a competing reaction, which has been given in the *Comments* column.

The *Method* column includes the method of generation and detection of the radical; other details are given under *Comments*. The references to Table 3 are listed by serial number assigned by the Radiation Chemistry Data Center and included in the RCDC Bibliographic Data Base.

## 7. Abbreviations and Symbols

| | |
|---|---|
| abs. | absorption |
| abstr. | abstraction |
| addn. | addition |
| alk. | alkaline |
| anal. | analysis |
| atm. | atmospheres ($1.013 \times 10^5$ N m$^{-2}$) |
| biol. | biological method, biological assay |
| bpy | 2,2′-bipyridine |
| *tert*-BuOH | *tert*-butyl alcohol |
| CTAB | hexadecyltrimethylammonium bromide |
| calcd. | calculated |
| chem. | chemical |
| c.k. | competition kinetics |
| concn. | concentration |
| condy. | conductivity |
| contg. | containing |
| cor. | corrected |
| cyt C | cytochrome C |
| DCIP | dichloroindophenol |
| DMSO | dimethyl sulfoxide |
| DNA | deoxyribonucleic acid |
| detd. | determined |
| d.k. | decay kinetics (decay of radical absorption and bleaching of substrate absorption) |
| *e*-r. | electron radiolysis |
| $\epsilon$ | extinction coefficient (molar absorptivity) |
| $E_a$ | activation energy |
| elec. | electrolysis, electrochemical method |
| EtOH | ethanol |
| esr | electron spin resonance |
| estd. | estimated |
| enz. | enzyme or enzymatic |
| FMN | flavin mononucleotide |
| f.p. | flash photolysis |
| formn. | formation |
| $\gamma$-r. | gamma radiolysis |
| $G$ | radiation yield (molecules per 100 eV) |
| $I$ | ionic strength |
| $K$ | equilibrium constant |
| $k$ | rate constant |
| $k_{\text{catalytic}}$ | rate constant for the overall catalyzed reaction |
| meas. | measured |
| MF | monoformazan |
| $NBT^{2+}$ | Nitro Blue Tetrazolium |
| obs. | observed |
| opt. | optical absorption |
| Pa | pascals (N m$^{-2}$) |
| p.b.k. | product buildup kinetics |
| phot. | photolysis |
| $pK_a$ | negative logarithm of the acid dissociation constant, e.g., where $AH + H_2O \rightleftharpoons A^- + H_3O^+$ |
| p.r. | pulse radiolysis |
| 2-PrOH | 2-propanol |
| Q | 1,4-benzoquinone (used in Table 3 as a competitor) |
| redn. | reduction |
| rel. | relative |
| satd. | saturated |
| SDS | sodium dodecylsulfate |
| s.f. | stopped flow |
| SOD | superoxide dismutase |
| soln. | solution |
| TMPO | trimethylpyrroline *N*-oxide |
| TNM | tetranitromethane |
| X-r. | X-radiolysis |

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TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 1 | **Americium(IV) ion** | | | | | |
| | $HO_2 + Am^{4+} \rightarrow H^+ + Am^{3+} + O_2$ | 1 | $6.4 \times 10^7$ | p.r., opt. | D.k. ($Am^{IV}$). $k$ varies with pH due to different degrees of hydrolysis of Am(IV) at each pH. | 771130 |
| | | 2 | $5.2 \times 10^7$ | | | |
| | | 3.2 | $5.0 \times 10^7$ | | | 77A243 |
| | | 4.4 | $2.7 \times 10^7$ | | | |
| 2 | **Borate ion** | | | | | |
| | $O_2^- + BO_3^{3-} \rightarrow$ | 10.0 | $<0.02$ | s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and $2 \times 10^{-4}$ mol L$^{-1}$ EDTA and 0.01–0.1 mol L$^{-1}$ borate; no reaction. | 770046 |
| 3 | **Tribromine ion** | | | | | |
| | $HO_2 + Br_3^- \rightarrow H^+ + Br_2^- + Br^- + O_2$ | 2–7 | $< 10^7$ | $e$–r., chem. | C.k. in formate-$Br_2$ soln.; rel. to $k(O_2^- + TNM) = 2 \times 10^9$. | 720308 |
| | | 2 | $(1 \pm 0.5) \times 10^8$ | p.r., opt. | C.k.; mechanistic anal. | 650383 |
| | $O_2^- + Br_3^- \rightarrow Br_2^- + Br^- + O_2$ | 7 | $(3.8 \pm 0.7) \times 10^9$ | $e$–r., chem. | C.k. in formate-$Br_2$ soln.; soln. contains 0.2 mol L$^{-1}$ $Br^-$; rel. to $k(O_2^- + TNM) = 2 \times 10^9$. | 720308 |
| 4 | **Dibromine radical ion** | | | | | |
| | $HO_2 + Br_2^- \rightarrow HO_2^- + Br_2$ | 2 | $6.5 \times 10^9$ | $\gamma$–r., chem. | C.k. in soln. contg. $10^{-4}$–1 mol L$^{-1}$ KBr; rel. to $HO_2 + Br_2$ and $Br_2^- + Br_2^-$. | 650055 |
| | | 2 | $(4.6 \pm 1.2) \times 10^9$ | p.r., opt. | D.k.; $k/\epsilon(Br_2^-) = (4.6 \pm 0.4) \times 10^5$ cm/s; more than one rate constant is involved in calcn. $k$ cor. using $\epsilon$(360 nm) = 9900 L mol$^{-1}$ cm$^{-1}$ for $Br_2^-$. | 650382 |
| | | 2 | $(1.6 \pm 0.5) \times 10^9$ | p.r., opt. | C.k.; obs. decay of $Br_2^-$ at 360 nm ($\epsilon$ = 9600 L mol$^{-1}$ cm$^{-1}$); data fitting. | 650383 |
| 5 | **Bromine** | | | | | |
| | $HO_2 + Br_2 \rightarrow Br + H^+ + Br^- + O_2$ | 2.1–2.9 | $(1.1 \pm 0.5) \times 10^8$ | $e$–r., chem. | C.k. in formate-$Br_2$ soln.; rel. to $k(O_2^- + TNM) = 2 \times 10^9$. | 720308 |
| | | ~1 | $1.5 \times 10^8$ | p.r., opt. | C.k.; indirect estimation; more than one rate constant is involved; uncertainty is two-fold. | 650382 |
| | $O_2^- + Br_2 \rightarrow Br_2^- + O_2$ | 7 | $(5.6 \pm 0.7) \times 10^9$ | $e$–r., chem. | C.k. in formate-$Br_2$ soln.; rel. to $k(O_2^- + TNM) = 2 \times 10^9$. | 720308 |
| 6 | **Hypobromous acid** | | | | | |
| | $O_2^- + HOBr \rightarrow Br + OH^- + O_2$ | 7 | $(9.5 \pm 0.8) \times 10^8$ | $e$–r., chem. | C.k. in formate-$Br_2$ soln.; rel. to $k(O_2^- + TNM) = 2 \times 10^9$. | 720308 |
| 7 | **Carbonic acid, p$K_a$ = 6.46, 10.3** | | | | | |
| | $HO_2/O_2^- + H_2CO_3/HCO_3^-/CO_3^{2-} \rightarrow HO_2^- + CO_3^-$ | 10.1 | $<0.04$ | s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and $10^{-4}$ mol L$^{-1}$ EDTA and $(0.1–2.5) \times 10^{-1}$ mol L$^{-1}$ carbonate; no reaction. | 770046 |
| | | 5.5 | $(1–2) \times 10^6$ | p.r., condy. | D.k. (rotating sector); $CO_2$ soln. | 720404 |
| 8 | **Carbonate radical ion**[a] | | | | | |
| | $O_2^- + CO_3^- \rightarrow CO_3^{2-} + O_2$ | | $(4 \pm 1) \times 10^8$ | f.p., opt. | D.k. in $O_2$-satd. soln. contg. 0.2 mol L$^{-1}$ $CO_3^{2-}$ at 260 nm and 600 nm; $\epsilon$ ($CO_3^-$) = 1860 at 600 nm and 200 at 260 nm and $\epsilon(O_2^-)$ = 1850 L mol$^{-1}$cm$^{-1}$ at 260 nm. | 700247 |
| | | 12.8 | $1.3 \times 10^8$ | f.p., opt. | D.k. at 260 and 600 nm; $\epsilon$(260) for $O_2^-$ = 900 and $\epsilon$(600) for $CO_3^-$ = 1830 L mol$^{-1}$ cm$^{-1}$. | 677012 |
| | | ~13 | $1.5 \times 10^9$ | p.r., opt. | D.k. at 600 as well as 260 nm; $\epsilon$(600) for $CO_3^-$ – $1.8 \times 10^3$, $\epsilon$(260) for $O_2^-$ – $1.22 \times 10^3$ L mol$^{-1}$ cm$^{-1}$. | 660001 |

[a]NOTE IN PROOF: A rate constant of $(3.0 \pm 0.5) \times 10^8$ has been determined by d.k. at 240 nm and 600 nm in carbonate solution at pH 10.1 (21 °C), with a small activation energy of 4.1 ± 0.7 kJ mol$^{-1}$ [private communication: G.V. Buxton and S. Dyster, 26 Nov. 1984].

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 9 | **Cerium(III) ion** $HO_2 + Ce^{3+} \rightarrow Ce^{4+} + H_2O_2$ | 0.4 | $(2.1 \pm 0.2) \times 10^5$ | p.r., opt. | P.b.k. at 320 nm, Ce(IV). | 741107 |
| 10 | **Cerium(IV) ion** $HO_2 + Ce^{4+} \rightarrow H^+ + Ce^{3+} + O_2$ | 0.4 | $\sim 2.7 \times 10^6$ | chem. | D.k.; flow technique; soln. cont. Ce(IV) + $H_2O_2$; calcd. rel. to $HO_2$ + Ce(III) using rate constant from [741107]. | 639017 |
| 11 | **Chloride ion** $O_2^- + Cl^- \rightarrow$ | 11.02 | $<0.014$ | p.r., opt. | D.k. at 240 nm in $O_2$-satd. formate soln., cor. for $O_2^-$ decay. Stopped-flow ($\gamma$-r. or vacuum uv photolysis) also used. Authors feel that no reaction occurs. | 80A049 |
| 12 | **Dichlorine radical ion** $HO_2 + Cl_2^- \rightarrow H^+ + Cl^- + Cl^- + O_2$ | $\sim 1$ | $(1.0 \pm 0.1) \times 10^9$ | p.r., opt. | Calcd. fit to d.k. at 340 nm in $O_2$-satd. soln. contg. 0.05 mol L$^{-1}$ $Cl^-$ and 0.15 mol L$^{-1}$ $HClO_4$; assumed $2k(Cl_2^- + Cl_2^-) = 4 \times 10^9$. | 80A378 |
| 13 | **Chlorine** $HO_2 + Cl_2 \rightarrow H^+ + Cl_2^- + O_2$ | 2 | $1 \times 10^9$ | p.r., opt. | D.k. at 260 nm ($HO_2$) as well as 340 nm ($Cl_2^-$) in oxygenated soln. contg. 0.19 mol L$^{-1}$ NaCl and 0.01 mol L$^{-1}$ $HClO_4$; $k(HO_2 + Cl_2^-)$ was taken to be identical to $k(HO_2 + Cl_2)$. | 81A227 |
| 14 | **Hypochlorous acid** $O_2^- + HOCl \rightarrow Cl^- + OH + O_2$ | 8.5–12.3 | $(7.5 \pm 0.38) \times 10^6$ | p.r., opt. | D.k. at 240 nm in $O_2$-satd. formate soln., $k$ calcd. from $k_{obs}$ vs pH study ($\sim 10^2 - 10^6$, see graph) and $K_{HClO} = 3.8 \times 10^8$ mol L$^{-1}$. Stopped-flow ($\gamma$-r. or vacuum uv photolysis) also used. | 80A049 |
| 15 | **Chlorite ion** $O_2^- + ClO_2^- \rightarrow$ | 7.4–11.3 | $<0.4$ | p.r., opt. | D.k. at 240 nm in $O_2$-satd. formate soln., cor. for $O_2^-$ decay. Stopped-flow ($\gamma$-r. or vacuum uv photolysis) also used. Authors feel no reaction occurs. | 80A049 |
| 16 | **Chlorine dioxide** $O_2^- + ClO_2 \rightarrow ClO_2^- + O_2$ | 12 | $(3.3 \pm 0.2) \times 10^9$ | p.r., opt. | D.k. at 360 nm in soln. contg. $10^{-2}$ mol L$^{-1}$ $ClO_2^-$ and $1.3 \times 10^{-2}$ mol L$^{-1}$ $H_2O_2$. | 81A242 |
| 17 | **Chlorate ion** $O_2^- + ClO_3^- \rightarrow$ | 11.1 | $<0.003$ | p.r., opt. | D.k. at 240 nm $O_2$-satd. formate soln., cor. for $O_2^-$ decay. Stopped-flow ($\gamma$-r. or vacuum uv photolysis) also used. Authors feel that no reaction occurs. | 80A049 |
| 18 | **Perchlorate ion** $O_2^- + ClO_4^- \rightarrow$ | 11.1 | | p.r., opt. | No reaction obs.; d.k. at 240 nm in $O_2$-satd. formate soln., cor. for $O_2^-$ decay. | 80A049 |
| 19 | **Bis(2,2'-bipyridine)cobalt(II) ion** $O_2^- + Co(bpy)_2^{2+} \rightarrow O_2Co(bpy)_2^+$ | | $1.9 \times 10^6$ | p.r., opt. | P.b.k.; pH not given but probably 7–8. | 771028 |
| 20 | **(2,3,9,10-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)cobalt(II) ion** $O_2^- + Co(tetraeneN_4)_2^{2+} \rightarrow O_2Co(tetraeneN_4)^+$ | 7–8 | $1.6 \times 10^9$ | p.r., opt. | P.b.k. | 771028 |
| 21 | **(5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)cobalt(II) ion** $O_2^- + Co(4,11\text{-}dieneN_4)_2^{2+} \rightarrow O_2Co(4.11\text{-}dieneN_4)^+$ | 7–8 | $1.4 \times 10^9$ | p.r., opt. | P.b.k. in soln. contg. $1.3 \times 10^{-3}$ mol L$^{-1}$ $O_2$ and 0.25 mol L$^{-1}$ *tert*-BuOH. | 771028 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 22 | **1,3,6,8,10,13,16,19-Octaazabicyclo[6.6.6]eicosanecobalt(II) ion** | | | | | |
| | $O_2^- + Co(sepulchrate)^{2+} \rightarrow Co(sepulchrate)^{3+} + H_2O_2$ | 11.3–12.6 | $(4.6 \pm 1.1) \times 10^7$ | f.p., opt. | P.b.k. at 480 nm in soln. contg. 2 mol L$^{-1}$ 2-PrOH, $5 \times 10^{-6}$ mol L$^{-1}$ benzophenone, $4 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.004–0.04 mol L$^{-1}$ KOH. | 83A304 |
| 23 | **Nitrilotriacetatocobaltate(II) ion** | | | | | |
| | $O_2^- + CoNTA^- \rightarrow (CoNTAO_2)^{2-}$ | 7 | $\leqslant 3 \times 10^8$ | p.r. | Prod. reacted with another molecule of solute $\rightarrow [CoNTAO_2CoNTA]^{3-}$, $k = 1.4 \times 10^7$. $\epsilon$(300 nm) $= 4.5 \times 10^3$ L mol$^{-1}$ cm$^{-1}$. | 79A255 |
| | $HO_2/O_2^- + CoNTA^- \rightarrow (CoNTAO_2)^{2-}$ | 5.0 | $(1.5 \pm 0.2) \times 10^8$ | p.r., opt. | Inner-sphere mechanism; spectral data for product given. | 78A436 |
| 24 | **Ethylenediaminetetraacetatocobaltate(II) ion** | | | | | |
| | $HO_2/O_2^- + CoEDTA^{2-} \rightarrow$ | 5.0 | $(2.0 \pm 0.3) \times 10^6$ | p.r., opt. | Inner-sphere mechanism; spectral data for product given. | 78A436 |
| 25 | **(2,3,9,10-Tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)cobalt(III) ion** | | | | | |
| | $HO_2/O_2^- + Co(tetraeneN_4)_2^{3+} \rightarrow$ | | $<10^5$ | p.r. | No reaction obs.; pH not given but probably 7–8. | 771028 |
| 26 | **Tetrakis(4-*N*-methylpyridyl)porphinecobalt(III) ion** | | | | | |
| | $HO_2/O_2^- + CoTMpyP^{5+} \rightarrow$ | 5.6 | $(1.4 \pm 0.1) \times 10^7$ | p.r., opt. | D.k. at 254 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ Na formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer. | 82A319 |
| | | 8.0 | $(9.0 \pm 0.9) \times 10^5$ | | | |
| | | 10.1 | $1 \times 10^5$ | enz, opt. | C.k., rel. to $k(O_2^- + NBT^{2+}) = 6 \times 10^4$, in soln. contg. 0.05 mol L$^{-1}$ carbonate buffer (pH 10.1) or borate buffer (pH 9.7). Obs. increase in absorbance at 560 nm ($NBT^{2+} \rightarrow$ formazan); $O_2^-$ produced in xanthine/xanthine oxidase system contg. catalase. | 79R111 |
| | | 9.7 | $4 \times 10^5$ | | | |
| 27 | **Tetrakis(*p*-sulfonatophenyl)porphinatocobaltate(III) ion** | | | | | |
| | $HO_2/O_2^- + CoTPPS^{3-} \rightarrow$ | 5.6 | $\leqslant 6 \times 10^5$ | p.r., opt. | D.k. at 254 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ Na formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer. | 82A319 |
| | | 8.0 | $\leqslant 1 \times 10^5$ | | | |
| 28 | **$\mu$-Amido-$\mu$-superoxidotetrakis(ethylenediamine)dicobalt(III) ion** | | | | | |
| | $HO_2 + O_2[Co(en)_2]_2NH_2^{4+} \rightarrow H^+ + O_2[Co(en)_2]_2NH_2^{3+} + O_2$ | 2.8–6.6 | $(3.0 \pm 0.5) \times 10^6$ | p.r., opt. | P.b.k. at 380 nm; calcd. from $k_{obs}$ vs pH; product is peroxido complex. | 80A139 |
| | $O_2^- + O_2[Co(en)_2]_2NH_2^{4+} \rightarrow O_2[Co(en)_2]_2NH_2^{3+} + O_2$ | 2.8–6.6 | $(5.8 \pm 0.3) \times 10^7$ | p.r., opt. | P.b.k. at 380 nm, calcd. from $k_{obs}$ vs pH; product is peroxido complex. | 80A139 |
| 29 | **Decakis(cyano)-$\mu$-superoxidodicobaltate(III) ion** | | | | | |
| | $HO_2 + O_2[Co(CN)_5]_2^{5-} \rightarrow H^+ + O_2[Co(CN)_5]_2^{6-} + O_2$ | 2.8–6.6 | $(4.7 \pm 0.3) \times 10^5$ | p.r., opt. | D.k. at 310 nm in soln. contg. 0.1 mol L$^{-1}$ formate ion studied as a function of pH; product is peroxido complex. | 80A139 |
| | $O_2^- + O_2[Co(CN)_5]_2^{5-} \rightarrow$ | 2.8–6.6 | | p.r., opt. | No reaction obs.; d.k. at 310 nm in solution contg. 0.1 mol L$^{-1}$ formate. | 80A139 |
| 30 | **Cyanocob(III)alamin** | | | | | |
| | $O_2^- + B12 \rightarrow$ | | | p.r. | No reaction obs.; pH not given but assumed to be 6–11. | 730116 |
| 31 | **Copper(I) ions** | | | | | |
| | $HO_2 + Cu^+ \rightarrow Cu^{2+} + H_2O_2$ | 2.3 | $2.3 \times 10^9$ | phot., opt. | Sector method; assume $k(HO_2 + Cu^{2+}) = 3.4 \times 10^7$ and $k(H_2O_2 + Cu^+) = 4.7 \times 10^3$. | 737514 |
| | | 2.3 | $6 \times 10^8$ | phot., opt. | Rotating sector; $k(HO_2 + Cu^+)/k(H_2O_2 + Cu^+) = 2.4$; soln. cont. $Cu^{2+}$ and 4.5 mol L$^{-1}$ $H_2O_2$; $I = 0.1$; see also [737514]. | 697082 |
| | $O_2^- + Cu^+ \rightarrow OH^- + Cu^{2+} + H_2O_2$ | ~3–6.5 | $10^{10}$ | p.r., opt. | D.k. at 245 nm in $Cu^{2+}$ soln. | 730112 |
| 32 | **Bis(1,10-phenanthroline)copper(I) ion** | | | | | |
| | $O_2^- + Cu(phen)_2^+ \rightarrow H_2O_2 + Cu(phen)_2^{2+}$ | 7.0 | $(2.95 \pm 0.3) \times 10^8$ | p.r., opt. | D.k. at 435 nm in soln. contg. 0.05 mol L$^{-1}$ formate, $10^{-3}$ mol L$^{-1}$ phosphate; 1,10-phenanthroline/$Cu^{2+}$ concn. = 2.0–2.5. | 83A299 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 33 | **Copper(II) ions** | | | | | |
| | $HO_2 + Cu^{2+} \rightarrow H^+ + Cu^+ + O_2$ | 0.8–2 | $\sim 10^8$ | p.r., opt. | D.k. at 245 nm. | 730112 |
| | $HO_2/O_2^- + Cu^{2+} \rightarrow H^+ + Cu^+ + O_2$ | 2.3 | $3.4 \times 10^7$ | phot., opt. | Sector method; $k(HO_2 + Cu^{2+})/k(O_2^- + Cu^{2+}) = 0.024$ | 737514 |
| | | 2.3 | $1.5 \times 10^7$ | f.p., opt. | D.k. at 254 nm. Rate may be too high by a factor of 2. | 620050 |
| | $O_2^- + Cu^{2+} \rightarrow Cu^+ + O_2$ | 8.0 | $(4.81 \pm 0.27) \times 10^9$ | p.r., opt. | D.k. at 245 nm ($O_2^-$); phosphate buffer. | 82A448 |
| | | 7.0 | $(8.1 \pm 0.5) \times 10^9$ | p.r., opt. | Observed rate; d.k. in soln. contg. $2 \times 10^{-3}$ mol L$^{-1}$ Na formate and $10^{-3}$ mol L$^{-1}$ phosphate buffer and $Cu(ClO_4)_2$. | 82A281 |
| | | 7.8 | $(2.7 \pm 0.2) \times 10^9$ | p.r., opt. | D.k. at 245 nm in $O_2$-satd. soln. contg. $10^{-5}$ mol L$^{-1}$ Na formate and $10^{-6}$ mol L$^{-1}$ $Cu^{2+}$; $k$ similar in presence of serum albumin. Observed rate. | 741163 |
| | | ~3–6.5 | $8 \times 10^9$ | p.r., opt. | D.k. at 245 nm. Rate determined from a broad pH range. | 730112 |
| 34 | **Amminecopper(II) ion** | | | | | |
| | $O_2^- + CuNH_3^{2+} \rightarrow$ | 5.8–8.5 | $(2.2 \pm 0.6) \times 10^9$ | p.r., opt. | D.k. at 248 nm; $I = 1$ | 761021 |
| 35 | **Bisamminecopper(II) ion** | | | | | |
| | $O_2^- + Cu(NH_3)_2^{2+} \rightarrow Cu(NH_3)_2^+ + O_2$ | 5.8–8.5 | $(2.2 \pm 0.8) \times 10^9$ | p.r., opt. | D.k. at 248 nm; $I = 1$. | 761021 |
| 36 | **Trisamminecopper(II) ion** | | | | | |
| | $O_2^- + Cu(NH_3)_3^{2+} \rightarrow$ | 5.8–8.5 | $(1.0 \pm 0.5) \times 10^9$ | p.r., opt. | D.k. at 248 nm; $I = 1$. | 761021 |
| 37 | **Tetraamminecopper(II) ion** | | | | | |
| | $O_2^- + Cu(NH_3)_4^{2+} \rightarrow$ | 5.8–8.5 | $(2 \pm 0.8) \times 10^8$ | p.r., opt. | D.k. at 248 nm; $I = 1$; authors feel value could be doubtful. | 761021 |
| 38 | **(5,7,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)copper(II) ion** | | | | | |
| | $HO_2/O_2^- + Cu(4,11\text{-dieneN}_4)^{2+} \rightarrow$ | | $<10^5$ | p.r. | No reaction. pH not given but probably 7–8. Limiting value. | 771028 |
| 39 | **Bis(1,10-phenanthroline)copper(II) ion** | | | | | |
| | $O_2^- + Cu(phen)_2^{2+} \rightarrow O_2 + Cu(phen)_2^+$ | 7.0 | $(1.93 \pm 0.07) \times 10^9$ | p.r., opt. | D.k. at 435 nm in soln. contg. 0.05 mol L$^{-1}$ formate, $10^{-3}$ mol L$^{-1}$ phosphate; 1,10-phenanthroline/$Cu^{2+}$ concn. = 2.0–2.5. $k$(catalytic) = $(5.1 \pm 0.9) \times 10^8$. | 83A299 |
| 40 | **Tetrakis(4-*N*-methylpyridyl)porphinecopper(II) ion** | | | | | |
| | $HO_2/O_2^- + CuTMpyP^{4+} \rightarrow$ | 5.6 | $\leqslant 6 \times 10^5$ | p.r., opt. | D.k. at 254 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ Na formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer. | 82A319 |
| | | 8.0 | $\leqslant 7 \times 10^4$ | | | |
| 41 | **Tetrakis-4-(*N,N,N*-trimethylammonio)phenylporphinecopper(II) ion** | | | | | |
| | $HO_2/O_2^- + CuTAPP^{4+} \rightarrow$ | 5.6 | $\leqslant 5 \times 10^6$ | p.r., opt. | D.k. at 254 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ Na formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer. | 82A319 |
| | | 8.0 | $\leqslant 1 \times 10^6$ | | | |
| | | | $<10^5$ | | Method (enz. or p.r.) and pH not given; $k$ = $k$(catalytic); reaction in 0.5 mol L$^{-1}$ carbonate buffer. | 82R172 |
| 42 | **Tetrakis(*p*-sulfonatophenyl)porphinatocuprate(II) ion** | | | | | |
| | $HO_2/O_2^- + CuTPPS^{4-} \rightarrow$ | 5.6 | $\leqslant 8 \times 10^5$ | p.r., opt. | D.k. at 254 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ Na formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer. | 82A319 |
| | | 8.0 | $\leqslant 5 \times 10^4$ | | | |
| 43 | **Formatocopper(II) ion** | | | | | |
| | $O_2^- + Cu(HCO_2)^+ \rightarrow O_2 + Cu(HCO_2)$ | | $(1.7 \pm 0.6) \times 10^9$ | p.r., opt. | D.k. at 248 nm in soln. contg. $10^{-4}$ mol L$^{-1}$ Cu(II) and $>10^{-3}$ mol L$^{-1}$ $HCO_2^-$; $I = 2$; pH not given but probably pH 6–7. | 761021 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 44 | **Copper(II) formate**<br>$O_2^- + Cu(HCO_2)_2 \rightarrow$ | | $3 \times 10^8$ | p.r., opt. | D.k. at 248 nm; correct to a factor of 2; calculated using stability constants; $I = 2$; pH not given but probably pH 6–7. | 761021 |
| 45 | **Trisformatocuprate(II) ion**<br>$O_2^- + Cu(HCO_2)_3^- \rightarrow$ | | $8.0 \times 10^8$ | p.r., opt. | D.k. at 248 nm; correct to a factor of 2; calculated using stability constants; $I = 2$; pH not given but probably pH 6–7. | 761021 |
| 46 | **Tetrakisformatocuprate(II) ion**<br>$O_2^- + Cu(HCO_2)_4^{2-} \rightarrow$ | | $(4.0 \pm 1.5) \times 10^8$ | p.r., opt. | D.k. at 248 nm; calcd. using stability constants; $I = 2$; pH not given but probably pH 6–7. | 761021 |
| 47 | **Bis(2-pyridinecarboxylato)copper(II)**<br>$HO_2/O_2^- + Cu(2\text{-}pyCO_2)_2 \rightarrow$ | | $2 \times 10^6$ | enz., opt. | D.k. at 250 nm (p.r.) in $N_2O/O_2$ (4:1) satd. soln. contg. 0.1 mol L$^{-1}$ formate gave $k$(catalytic) $= 1.4 \times 10^8$; pH not given, probably 8.5. | 83A209 |
| 48 | **DL-Alaninatocopper(II) ion**<br>$HO_2/O_2^- + Cu(Ala)^+ \rightarrow$ | 7.4 | $(2.8\text{–}3.5) \times 10^6$ | p.r., opt. | D.k. at 280 nm in soln. contg. $10^{-2}$ mol L$^{-1}$ alanine, $5 \times 10^{-3}$ mol L$^{-1}$ formate and $(1\text{–}3) \times 10^{-4}$ mol L$^{-1}$ $Cu^{2+}$. | 761021 |
| 49 | **Alanylhistidinatocopper(II)**<br>$O_2^- + Cu(AlaHis) \rightarrow$ | 8.0 | $(8.75 \pm 0.41) \times 10^7$ | p.r., opt. | D.k. at 245 nm ($O_2^-$); phosphate buffer. | 82A448 |
| 50 | **Glutamatocopper(II) ion**<br>$HO_2/O_2^- + Cu(Glu)^+ \rightarrow$ | 7.1 | $(1\text{–}2) \times 10^6$ | p.r., opt. | D.k. at 280 nm in soln. contg. (1 or 3) $\times$ $10^{-4}$ mol L$^{-1}$ $Cu^{2+}$ and 0.1 mol L$^{-1}$ glutamate. | 761021 |
| 51 | **Glycinatocopper(II) ion**<br>$O_2^- + Cu(Gly)^+ \rightarrow$ | 7.9 | $2.1 \times 10^6$ | p.r., opt. | D.k. at 280 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ formate and $2 \times 10^{-3}$ mol L$^{-1}$ glycine; $k = \sim 1 \times 10^6$ with 1 mol L$^{-1}$ glycine at pH 6 (d.k. at 248 nm). | 761021 |
| | | 8.0 | $(4.1 \pm 0.6) \times 10^6$ | p.r., opt. | D.k. at 275 nm in $N_2O$–$O_2$–satd. soln. contg. $5 \times 10^{-2}$ mol L$^{-1}$ glycine and $10^{-4}$ mol L$^{-1}$ $Cu(ClO_4)_2$; same when formate was added. | 761082 |
| 52 | **Glycylglycinatocopper(II) ion**<br>$HO_2/O_2^- + Cu(GlyGly)^+ \rightarrow$ | 6.7 | $(1.9\text{–}2.0) \times 10^7$ | p.r., opt. | D.k. at 280 nm in soln. contg. $1\text{–}2 \times 10^{-4}$ mol L$^{-1}$ $Cu^{2+}$ and $10^{-2}$ mol L$^{-1}$ glycylglycine. | 761021 |
| 53 | **Bis(glycylhistidinato)cuprate(II) ion**<br>$O_2^- + Cu(GlyHis)_2^{2-} \rightarrow$ | 7.8 | $(3.0 \pm 0.2) \times 10^8$ | p.r., opt. | D.k. at 245 nm in $O_2$–satd. soln. contg. $10^{-3}$ mol L$^{-1}$ Na formate and $10^{-5}$–$10^{-6}$ mol L$^{-1}$ $Cu^{2+}$; $k$ similar in presence of serum albumin. | 741163 |
| 54 | **Bis(glycylhistidylleucinato)cuprate(II) ion**<br>$O_2^- + Cu(GlyHisLeu)_2^{2-} \rightarrow$ | 7.8 | $(2.1 \pm 0.2) \times 10^8$ | p.r., opt. | D.k. at 245 nm in $O_2$–satd. soln. contg. formate ion and $\sim 10^{-6}$ mol L$^{-1}$ complex; $k$ $= 1 \times 10^8$ in presence of bovine serum albumin. Concn. varied giving true pseudo first-order conditions. | 75A243<br>741163 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 55 | **Bis(histidinato)copper(II) ion, conjugate monoacid** $HO_2/O_2^- + Cu(His)_2H^+ \rightarrow$ | 2–7 | $(3.4 + 0.9) \times 10^8$ | p.r., opt. | D.k. at 250 nm in soln. contg. 0.1 mol L$^{-1}$ formate, $4 \times 10^{-4}$ mol L$^{-1}$ histidine and $1\text{–}100 \times 10^{-6}$ mol L$^{-1}$ Cu(II) acetate; $k = k_{catalytic}$. | 80A175 |
| 56 | **Histidylalaninatocopper(II)** $O_2^- + Cu(HisAla) \rightarrow$ | 8.0 | $(4.52 \pm 0.34) \times 10^9$ | p.r., opt. | D.k. at 245 nm ($O_2^-$); phosphate buffer. | 82A448 |
| 57 | **Histidylphenylalaninatocopper(II)** $O_2^- + Cu(HisPhe) \rightarrow$ | 8.0 | $(3.57 \pm 0.38) \times 10^9$ | p.r., opt. | D.k. at 245 nm ($O_2^-$); phosphate buffer. | 82A448 |
| 58 | **Histidyltyrosinatocopper(II)** $O_2^- + Cu(HisTyr) \rightarrow$ | 8.0 | $(2.42 \pm 0.23) \times 10^9$ | p.r., opt. | D.k. at 245 nm ($O_2^-$); phosphate buffer. | 82A448 |
| 59 | **Histidylvalinatocopper(II)** $O_2^- + Cu(HisVal) \rightarrow$ | 8.0 | $(2.22 \pm 0.27) \times 10^9$ | p.r., opt. | D.k. at 245 nm ($O_2^-$); phosphate buffer. | 82A448 |
| 60 | **L-Hydroxyprolinecopper(II) ion** $HO_2/O_2^- + Cu(Hyp)^+ \rightarrow$ | 8.1 | $1.2 \times 10^6$ | p.r., opt. | D.k. at 270 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ formate, $2 \times 10^{-3}$ mol L$^{-1}$ hydroxyproline and $5 \times 10^{-5}$ mol L$^{-1}$ $Cu^{2+}$; $k = 1.0 \times 10^6$ with $10^{-4}$ mol L$^{-1}$ $Cu^{2+}$ and $9.0 \times 10^5$ with $10^{-4}$ mol L$^{-1}$ $Cu^{2+}$ and $10^{-2}$ mol L$^{-1}$ hydroxyproline at pH 7.7. | 761021 |
| 61 | **Bis(lysinato)copper(II)** $O_2^- + Cu(Lys)_2 \rightarrow$ | 7.8 | $(5.6 \pm 1) \times 10^8$ | p.r., opt. | D.k. at 245 nm in $O_2$-satd. soln. contg. $10^{-3}$ mol L$^{-1}$ Na formate and $10^{-5}$–$10^{-6}$ mol L$^{-1}$ $Cu^{2+}$; $k$ similar in presence of serum albumin. | 741163 |
| 62 | **L-Methioninatocopper(II) ion** $HO_2/O_2^- + Cu(Met)^+ \rightarrow$ | 7.1<br>7.8 | $5.6 \times 10^6$<br>$6.8 \times 10^6$ | p.r., opt. | D.k. at 280 nm in soln. contg. $5 \times 10^{-2}$ mol L$^{-1}$ methionine and $10^{-4}$ mol L$^{-1}$ $Cu^{2+}$; at pH 7.8 $k = 8 \times 10^6$ with $[Cu^{2+}] = 2 \times 10^{-4}$ and at pH 7.1 $k = 4.8 \times 10^6$ with $[Cu^{2+}] = 3 \times 10^{-4}$ mol L$^{-1}$. | 761021 |
| 63 | **Phenylalanylhistidinatocopper(II)** $HO_2/O_2^- + Cu(PheHis) \rightarrow$ | 8.0 | $(9.90 \pm 1.20) \times 10^4$ | p.r., opt. | D.k. at 245 nm ($O_2^-$); phosphate buffer. | 82A448 |
| 64 | **L–Prolinatocopper(II) ion** $HO_2/O_2^- + Cu(Pro)^+ \rightarrow$ | 7.5 | $5 \times 10^5$ | p.r., opt. | D.k. at 270 nm in soln. contg. $10^{-4}$ mol L$^{-1}$ $Cu^{2+}$ and $10^{-3}$ mol L$^{-1}$ proline. | 761021 |
| 65 | **Bis(tyrosinato)copper(II)** $O_2^- + Cu(Tyr)_2 \rightarrow$ | 7.4-7.8 | $(1.0 \pm 0.1) \times 10^9$ | p.r., opt. | D.k. at 245 nm in $O_2$-satd. soln. contg. formate ion and $\sim 10^{-6}$ mol L$^{-1}$ complex; same result in presence of 0.11 g L$^{-1}$ bovine serum albumin. | 75A243 |
| 66 | **L-Valinatocopper(II) ion** $HO_2/O_2^- + Cu(Val)^+ \rightarrow$ | 6.2<br>8.1 | $2.4 \times 10^8$<br>$1.7 \times 10^6$ | p.r., opt. | D.k. at 280 nm in soln. contg. $10^{-4}$ mol L$^{-1}$ $Cu^{2+}$ and $0.5 \times 10^{-3}$ (pH 8.1) or $10^{-2}$ mol L$^{-1}$ (pH 6.2) valine. | 761021 |
| 67 | **Valylhistidinatocopper(II)** $HO_2/O_2^- + Cu(ValHis) \rightarrow$ | 8.0 | $(1.01 \pm 0.16) \times 10^5$ | p.r., opt. | D.k. at 245 nm ($O_2^-$); phosphate buffer. | 82A448 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 68 | **Ethylenediaminetetraacetatocuprate(II) ion** | | | | | |
| | $O_2^- + CuEDTA^{2-} \rightarrow$ | 6.8–9.8 | $<10^5$ | p.r., opt. | Soln. cont. $2 \times 10^{-8}$ mol L$^{-1}$ $Cu^{2+}$, $10^{-6}$ mol L$^{-1}$ EDTA. | 82A281 |
| 69 | **Bis(salicylato)copper(II)** | | | | | |
| | $O_2^- + Cu(Sal)_2 \rightarrow$ | 7.5 | $(1.64 \pm 0.15) \times 10^9$ | p.r., opt. | D.k. at 250 nm in $O_2$-satd. soln. contg. formate and $1–5 \times 10^{-6}$ mol L$^{-1}$ $Cu^{II}$. | 78A309 |
| 70 | **Bis(diisopropylsalicylato)copper(II)** | | | | | |
| | $O_2^- + Cu(2\text{-}PrSal)_2 \rightarrow$ | 7.5 | $(2.4 \pm 0.12) \times 10^9$ | p.r., opt. | D.k. at 250 nm in $O_2$-satd. soln. contg. formate and $2.2–5.4 \times 10^{-6}$ mol L$^{-1}$ $Cu^{II}$. | 78A309 |
| 71 | **Bis(acetylsalicylato)copper(II)** | | | | | |
| | $O_2^- + Cu(AcSal)_2 \rightarrow$ | 7.5 | $(0.96 \pm 0.20) \times 10^9$ | p.r., opt. | D.k. at 250 nm in $O_2$—satd. soln. contg. formate and $1.1–8.4 \times 10^{-6}$ mol L$^{-1}$ $Cu^{II}$. | 78A309 |
| 72 | **Bis(*p*-aminosalicylato)copper(II)** | | | | | |
| | $O_2^- + Cu(NH_2Sal)_2 \rightarrow$ | 7.5 | $(0.79 \pm 0.16) \times 10^9$ | p.r., opt. | D.k. at 250 nm in $O_2$-satd. soln. contg. formate and $2–10 \times 10^{-6}$ mol L$^{-1}$ $Cu^{II}$. | 78A309 |
| 73 | **Bis[copper(2-[2-(pyridyl)ethyliminomethyl]pyridine)]imidazole bridged complex** | | | | | |
| | $O_2^- + Cu(pip)ImCu(pip)^{3+} \rightarrow$ | ~8 | $(1.7 \pm 1) \times 10^8$ | p.r., opt. | D.k. at 250 nm in soln. contg. $10^{-2}$ mol L$^{-1}$ formate. | 81A430 |
| 74 | **Copper(2-[2-(pyridyl)ethyliminomethyl]pyridine) zinc(2-[2-(pyridyl)ethyliminomethyl]pyridine) imidazole bridged complex** | | | | | |
| | $O_2^- + Cu(pip)ImZn(pip)^{3+} \rightarrow$ | ~8 | $(5.9 \pm 1.0) \times 10^8$ | p.r., opt. | D.k. at 250 nm in soln. contg. $10^{-2}$ mol L$^{-1}$ formate | 81A430 |
| 75 | **Penicillaminecopper complex** | | | | | |
| | $HO_2/O_2^- + Cu_{14}(Pen)_{12}Cl^{5-} \rightarrow$ | 7.0 | $(4.5 \pm 0.5) \times 10^8$ | p.r., opt. | D.k. at 250 nm in $O_2$-satd. soln. contg. $10^{-2}$ mol L$^{-1}$ formate and $10^{-6}–10^{-5}$ mol L$^{-1}$ penicillamine. | 79A072 |
| | | 3.1 | $(9.2 \pm 1.5) \times 10^8$ | p.r., opt. | D.k. in soln. contg. 0.05 mol L$^{-1}$ formate and 0.91–9.1 $\times 10^{-6}$ mol L$^{-1}$ Cu penicillamine. | 79A455 |
| | | 5.0 | $(3.15 \pm 0.82) \times 10^9$ | | | |
| | | 7.0 | $(6.8 \pm 1.5) \times 10^8$ | | | |
| | | 8.9 | $(5.1 \pm 0.6) \times 10^8$ | | | |
| | | | $4.2 \times 10^8$ | | 1:1 in EDTA ($k = 1.1 \times 10^8$ in 1:10 EDTA, ten-fold excess of EDTA); $k = 7.8 \times 10^8$ in 1:1 KCN ($k = 8.2 \times 10^7$ in 1:10 KCN, ten-fold excess of KCN); conditions and pH not given. | 81R192 |
| | | | See comment. | | $[Cu^I_8Cu^{II}_6(D\text{-penicillamine})_{12}Cl]^{5-}$ does not catalyze $O_2^-$ dismutation but rather decomposes to simpler Cu complexes which are active. | 80R189 |
| | $O_2^- + Cu_{14}(Pen)_{12}Cl^{5-} \rightarrow$ | 3–9 | $2.0 \times 10^8$ | p.r., opt. | D.k. (see 79A072, 79R055) in presence of $10^{-8}–10^{-6}$ mol L$^{-1}$ Cu complex; reaction thought to involve sulfur: $Cu(I)\dot{S}R + O_2^- \rightarrow Cu(I)^-SR + O_2$ and $Cu(I)^-SR + O_2^- \rightarrow Cu(II)\dot{S}R + O_2^{2-}$. Slight variation in $k_{obs}$ with pH. | 80Z241 |
| | | | $(1.54 \pm 0.5) \times 10^9$ | p.r., opt. | D.k. Refer to [79A072] for experimental details. | 79R055 |
| 76 | **Copper indomethacin** | | $3.2 \times 10^9$ | | 1:1 in EDTA ($k < 10^7$ in 1:10 EDTA, ten-fold excess of EDTA); $k = 4.1 \times 10^9$ in 1:1 KCN ($k < 10^7$ in 1:10 KCN, ten-fold excess of KCN); conditions and pH not given. | 81R192 |
| | $HO_2/O_2^- + Cu_2I_4 \rightarrow$ | | | | | |
| | $O_2^- + Cu_2I_4 \rightarrow$ | 7.0 | $(6.0 \pm 0.3) \times 10^9$ | p.r., opt. | D.k. at 250 nm in soln. contg. $10^{-2}$ mol L$^{-1}$ formate; in 50/50 (v/v) acetonitrile-water $k = (1.1 \pm 0.4) \times 10^9$. | 80A201 |
| | | 6.6 | $6 \times 10^9$ | p.r., opt. | D.k. in soln. contg. 0.05 mol L$^{-1}$ formate and 9.8–83 $\times 10^{-8}$ mol L$^{-1}$ Cu indomethacin. | 79A455 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 77 | **Iron(II) ion** | | | | | |
| | $HO_2 + Fe^{2+} \rightarrow Fe^{3+}\cdot HO_2^-$ | 1 | $(1.2 \pm 0.5) \times 10^6$ | p.r., opt. | P.b.k. at 250 nm at 25°C; $I = 1.0$; $k = 9.1 \times 10^5$ at 20°C; $E_a = 10.0 \pm 1.0$ kcal/mol (42 kJ/mol); supercedes [640090] and [690434]. | 730038 |
| 78 | **Tris(1,10-phenanthroline)iron(II) ion** | | | | | |
| | $O_2^- + Fe(phen)_3^{2+} \rightarrow$ | 10.1 | $1 \times 10^5$ | enz., opt. | C.k.; rel. to $k(O_2^- + NBT^{2+}) = 6 \times 10^4$. | 79A018 |
| 79 | **Bis(4,7-diphenyl-1,10-phenanthroline)iron(II) ion** *(Bathophenanthroline)* | | | | | |
| | $O_2^- + Fe(Ph_2phen)_2^{2+} \rightarrow$ | 7.0 | $<2.8 \times 10^5$ | p.r., opt. | D.k. at 310 nm in 0.1 mol L$^{-1}$ Na formate contg. $10^{-1}$ mol L$^{-1}$ phosphate buffer. | 82A449 |
| 80 | **Dicyanotetrakis(4-*N*-methylpyridyl)porphineiron(II) ion** | | | | | |
| | $O_2^- + FeTMpyP(CN)_2^{2+} \rightarrow O_2 + FeTMpyP(CN)_2^{3+}$ | 10.2 | $(3.1 \pm 0.6) \times 10^6$ | p.r., opt. | Calcd. from equil. concn. formed in $O_2$-satd. soln. of $Fe^{III}$ complex and reduced ($Fe^{II}$) complex; $k_{obs} = (1.7 \pm 0.3) \times 10^6$ in presence of formate. | 82A119 |
| 81 | **Tetrakis(4-*N*-methylpyridyl)porphineiron(II)-diimidazole complex** | | | | | |
| | $HO_2/O_2^- + FeTMpyP(Im)_2^{4+} \rightarrow OH^- + H_2O_2 + FeTMpyP(Im)_2^{5+}$ | | $(3.8 \pm 0.7) \times 10^6$ | p.r., opt. | P.b.k. Measured in absence of formate. $k$ in presence of formate = $(1.3 \pm 0.6) \times 10^6$. Probably pH 8.0. | 82A119 |
| 82 | **Tetrakis(4-*N*-methylpyridyl)porphineiron(II)-dihistidine complex** | | | | | |
| | $HO_2/O_2^- + FeTMpyP(His)_2^{4+} \rightarrow OH^- + H_2O_2 + FeTMpyP(His)_2^{5+}$ | | $(3.1 \pm 0.5) \times 10^6$ | p.r., opt. | P.b.k. Measured in absence of formate. $k$ in presence of formate = $(1.7 \pm 0.3) \times 10^6$. Probably pH 8.0. | 82A119 |
| 83 | **Ferrocyanide ion** | | | | | |
| | $HO_2 + Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + HO_2^-$ | 0.46–4.37 | $(3.0 \pm 1.5) \times 10^4$ | p.r., opt. | P.b.k. at 420–460 nm; pH effects obs. | 720431 |
| | | ~2 | $1.64 \times 10^5$ | p.r., opt. | P.b.k. at 420 nm (ferricyanide). Soln. cont. $5 \times 10^{-3}$ mol L$^{-1}$ ferrocyanide. | 650007 |
| 84 | **Potassium hexacyanoferrate(II) ion** | | | | | |
| | $HO_2 + KFe(CN)_6^{3-} \rightarrow$ | 0–6.5 | $(3.0 \pm 1.5) \times 10^4$ | p.r., opt. | P.b.k. at 420 nm. | 720431 |
| 85 | **Hydrogen hexacyanoferrate(II) ion** | | | | | |
| | $HO_2 + HFe(CN)_6^{3-} \rightarrow$ | 0.46–4.37 | $(1.4 \pm 0.1) \times 10^5$ | p.r., opt. | P.b.k. at 420–460 nm. | 720431 |
| 86 | **Dihydrogen hexacyanoferrate(II) ion** | | | | | |
| | $HO_2 + H_2Fe(CN)_6^{2-} \rightarrow$ | 0.46–4.37 | $(1.0 \pm 0.3) \times 10^4$ | p.r., opt. | P.b.k. at 420–460 nm. | 720431 |
| 87 | **Ethylenediaminetetraacetatoferrate(II) ion** | | | | | |
| | $O_2^- + FeEDTA^{2-} \rightarrow Fe(O_2)EDTA^{3-}$ | 10.4 | $\sim 8 \times 10^6$ | s.f., opt. | P.b.k. at 520 nm; soln. cont. $10^{-6}$ mol L$^{-1}$ complex; $I = 1$. | 83A163 |
| | | 10.4 | $(3 \pm 0.3) \times 10^6$ | p.r., opt. | P.b.k. at 310–350 nm in soln. contg. 0.1 mol L$^{-1}$ Na formate. | 82A449 |
| | | 7.8 | $2 \times 10^6$ | p.r., opt. | D.k. at 250 nm. | 82A446 |
| | | 10.1 | $3 \times 10^5$ | enz., opt. | C.k.; rel. to $k(O_2^- + NBT^{2+}) = 6 \times 10^4$. | 79A018 |
| | | 9.7 | $4 \times 10^5$ | enz, opt. | C.k.; rel. to $k(O_2^- + NBT^{2+}) = 6 \times 10^4$, in 0.05 mol L$^{-1}$ borate buffer. Obs. increase in absorbance at 560 nm ($NBT^{2+} \rightarrow$ formazan); $O_2^-$ produced in xanthine/xanthine oxidase system contg. catalase. | 79R111 |
| | | 9–10 | $(2 \pm 0.3) \times 10^6$ | p.r., opt. | P.b.k. at 300 nm in air-satd. soln. contg. $10^{-2}$ mol L$^{-1}$ Na formate and 0.5–2 $\times 10^{-3}$ mol L$^{-1}$ carbonate buffer; at pH 11–12 $k$ is 50% higher; above pH 9 the substrate is a hydroxo complex. | 771088 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 88 | **Diethylenetriaminepentaacetatoferrate(II) ion** *(Detapac $Fe^{2+}$)* | | | | | |
| | $O_2^- + FeDTPA^{3-} \rightarrow$ | 7.0 | $(2 \pm 0.5) \times 10^7$ | p.r., opt. | P.b.k. at 310 nm in 0.1 mol L$^{-1}$ Na formate contg. $10^{-1}$ mol L$^{-1}$ phosphate buffer. | 82A449 |
| | | 10.1 | $1 \times 10^5$ | enz., opt. | C.k.; rel. to $k(O_2^- + NBT^{2+}) = 6 \times 10^4$. | 79A018 |
| 89 | **Adenosine triphosphate-iron(II) complex** | | | | | |
| | $O_2^- + Fe^{II}ATP \rightarrow$ | 7.0 | $(1.1 \pm 0.1) \times 10^6$ | p.r., opt. | P.b.k. at 310 nm in 0.1 mol L$^{-1}$ Na formate contg. $10^{-1}$ mol L$^{-1}$ phosphate buffer. | 82A449 |
| 90 | **Iron(III) ions** | | | | | |
| | $HO_2 + Fe^{3+} \rightarrow H^+ + Fe^{2+} + O_2$ | 1.51 | $2 \times 10^4$ | p.r., opt. | In $H_2SO_4$ soln.; calcd. rel. to $k(HO_2 + Fe^{2+}) = 1 \times 10^6$; in $HClO_4$ soln. $k = 2.1 \times 10^5$ and $1.0 \times 10^6$, resp. at pH 1.51 and 2.74. | 690413 |
| | | 2.74 | $3.1 \times 10^5$ | | | |
| | | 1 | $\sim 4 \times 10^5$ | $\gamma$-r., chem. | C.k. using $k(HO_2 + Fe^{2+})/k(HO_2 + Fe^{3+}) = 30[H^+]$ from data in [730038]. | 690642 |
| | | | $6.6 \times 10^3$ | $\gamma$-r., chem. | C.k.; calcd. using data from [730038]; rel. to $HO_2 + Fe^{2+} = 1.2 \times 10^6$; 0.25 mol L$^{-1}$ $H_2SO_4$. | 600102 |
| | | 2.1 | $1.2 \times 10^5$ | $\gamma$-r., chem. | C.k.; calcd. using data from [730038]; rel. to $HO_2 + Fe^{2+} = 1.2 \times 10^6$. | 580004 |
| | | 0.4 | $< 1.2 \times 10^4$ | | | |
| | | 2.7 | $3.6 \times 10^5$ | $\gamma$-r., chem. | C.k.; calcd. using data from [730038]; rel. to $HO_2 + Fe^{2+} = 1.2 \times 10^6$. | 570010 |
| | | 2.0 | $1.32 \times 10^5$ | | | |
| 91 | **Bis(4,7-diphenyl-1,10-phenanthrolineiron(III) ion** | | | | | |
| | $O_2^- + Fe(Ph_2phen)_2^{3+} \rightarrow$ | 7.0 | $< 4 \times 10^4$ | p.r., opt. | D.k. at 300–320 nm in 0.1 mol L$^{-1}$ Na formate contg. $10^{-1}$ mol L$^{-1}$ phosphate buffer. | 82A449 |
| 92 | **Tetrakis(4-*N*-methylpyridyl)porphineiron(III) ion** | | | | | |
| | $O_2^- + FeTMpyP^{5+} \rightarrow$ $[FeTMpyP\text{-}O_2]^{4+}$ | 5.6 | $(1.7 \pm 0.2) \times 10^9$ | p.r., opt. | D.k. at 420 as well as p.b.k. at 445 nm in $O_2$-satd. soln. contg. 0.1 mol L$^{-1}$ *tert*-BuOH; $k_{obs} = 3.8 \times 10^8$ at pH 8.0 and $3.1 \times 10^8$ at pH 5.6 in the presence of 0.1 mol L$^{-1}$ formate; at pH 10.1 in soln. contg. 0.05 mol L$^{-1}$ carbonate $k = (3.9 \pm 0.4) \times 10^8$. | 82A119 |
| | | 8.0 | $(2 \pm 0.2) \times 10^9$ (cor. for $I$) | | | |
| | | 5.6 | $(2.2 \pm 0.2) \times 10^8$ | p.r., opt. | D.k. at 254 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ Na formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer. | 82A319 |
| | | 8.0 | $(3.0 \pm 0.3) \times 10^8$ | | | |
| | | 7.8 | $\sim (7 \pm 2) \times 10^8$ | p.r., opt. | D.k. at 350 nm (also obs. at 580 nm) indicated different product from $e_{aq}^-$ or $CO_2^-$ reaction, interpreted as adduct formn.; obs. rate includes aggregates of Fe complex. | 81A207 |
| | | 7.8 | $\sim 3 \times 10^7$ | p.r., opt. | D.k. at 280 and 296 nm in $O_2$-satd. soln. contg. $10^{-3}$ mol L$^{-1}$ phosphate buffer, $5 \times 10^{-3}$ mol L$^{-1}$ formate and $2 \times 10^{-4}$ mol L$^{-1}$ EDTA. | 81A207 |
| | | 10.1 | $3 \times 10^7$ | enz., opt. | C.k.; rel. to $k(O_2^- + NBT^{2+}) = 6 \times 10^4$; obs. decrease in redn. of nitro blue tetrazolium to formazan at 560 nm; biphasic, $k = 2 \times 10^6$ in phase II. | 79A018 |
| | | 9.7 | $1 \times 10^7$ | enz, opt. | C.k.; rel. to $k(O_2^- + NBT^{2+}) = 6 \times 10^4$, in 0.05 mol L$^{-1}$ borate buffer at pH 9.7 (0.05 mol L$^{-1}$ carbonate buffer at pH 10.1). Obs. increase in absorbance at 560 nm ($NBT^{2+} \rightarrow$ formazan); $O_2^-$ produced in xanthine/xanthine oxidase system contg. catalase; imidazole complex had similar reactivity. | 79R111 |
| | | 10.1 | $3 \times 10^7$ | | | |
| 93 | **Tetrakis(4-*N*-methylpyridyl)porphineiron(III)-superoxide complex** | | | | | |
| | $O_2^- + [FeTMpyP\text{-}O_2]^{4+} \rightarrow OH^- + OH^- + FeTMpyP^{5+} + H_2O_2$ | 8.1 | $(2.3 \pm 0.3) \times 10^9$ | p.r., opt. | Calcd. from equil. concn. formed in $O_2$-satd. soln. of $Fe^{III}$ complex and $O_2^-$ adduct ($I = 10^{-3}$); in presence of formate $k = (7.6 \pm 1.0) \times 10^8$. | 82A119 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 94 | **Dicyanotetrakis(4-*N*-methylpyridyl)porphineiron(III) ion** | | | | | |
| | $O_2^- + FeTMpyP(CN)_2^{3+} \rightarrow FeTMpyP(CN)_2^{2+} + O_2$ | 10.2 | $(2.0 \pm 0.2) \times 10^6$ | p.r., opt. | D.k. as 435 as well as p.b.k. at 470 nm in soln. contg. $2.0 \times 10^{-3}$ mol L$^{-1}$ KCN and $1\text{–}5 \times 10^{-5}$ mol L$^{-1}$ $Fe^{III}$ complex. | 82A119 |
| 95 | **Tetraakis(4-*N*-methylpyridyl)porphineiron(III)-diimidazole complex** | | | | | |
| | $O_2^- + FeTMpyP(Im)_2^{5+} \rightarrow FeTMpyP(Im)_2^{4+} + O_2$ | 8.0 | $(1.0 \pm 0.1) \times 10^6$ | p.r., opt. | P.b.k at 450 nm in $O_2$-satd. soln. contg. $1\text{–}2.5 \times 10^{-5}$ mol L$^{-1}$ $Fe^{III}$ TMpyP and $4 \times 10^{-2}$ mol L$^{-1}$ imidazole and 0.5 mol L$^{-1}$ formate. | 82A119 |
| | | 9.7 | $9 \times 10^5$ | enz., opt. | C.k. in 0.05 mol L$^{-1}$ borate buffer; rel. to $k(O_2^- + NBT^{2+}) = 6 \times 10^4$. | 79R111 |
| 96 | **Tetrakis(4-*N*-methylpyridyl)porphineiron(III)-dihistidine complex** | | | | | |
| | $HO_2/O_2^- + FeTMpyP(His)_2^{5+} \rightarrow FeTMpyP(His)_2^{4+} + O_2$ | 8.0 | $(1.2 \pm 0.1) \times 10^6$ | p.r., opt. | P.b.k. | 82A119 |
| 97 | **Tetrakis-4-(*N,N,N*-trimethylammonio)phenylporphineiron(III) ion** | | | | | |
| | $HO_2/O_2^- + FeTAPP^{5+} \rightarrow$ | | See comment | | Method (enz. or p.r.) or pH not given; $k$(catalytic) $= 5 \times 10^5$; reaction in 0.5 mol L$^{-1}$ carbonate buffer. | 82R172 |
| 98 | **Tetrakis(*p*-sulfonatophenyl)porphineferrate(III) ion** | | | | | |
| | $HO_2/O_2^- + FeTPPS^{3-} \rightarrow$ | 5.6 | $(8 \pm 0.8) \times 10^6$ | p.r., opt. | D.k. at 254 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ Na formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer and 0.1 mol L$^{-1}$ NaCl. | 82A319 |
| | | 8.0 | $(1.2 \pm 0.1) \times 10^6$ | | | |
| | $O_2^- + FeTPPS^{3-} \rightarrow$ | 9.7 | $4 \times 10^5$ | enz, opt. | C.k.; rel. to $k(O_2^- + NBT^{2+}) = 6 \times 10^4$, in 0.05 mol L$^{-1}$ borate buffer at pH 9.7 (0.05 mol L$^{-1}$ carbonate buffer at pH 10.1). Obs. increase in absorbance at 560 nm ($NBT^{2+} \rightarrow$ formazan); $O_2^-$ produced in xanthine/xanthine oxidase system contg. catalase; BSA and imidazole complexes had similar reactivity. | 79R111 |
| | | 10.1 | $6 \times 10^5$ | | | |
| 99 | **Tetrakis(*p*-sulfonatophenyl)porphineferrate(III)-diimidazole complex** | | | | | |
| | $O_2^- + FeTPPS(Im)_2^{3-} \rightarrow$ | 9.7 | $3 \times 10^5$ | enz. | C.k. in 0.05 mol L$^{-1}$ borate buffer; rel. to $k(O_2^- + NBT^{2+}) = 6 \times 10^4$. | 79R111 |
| 100 | **Tetrakis(*p*-sulfonatophenyl)porphineferrate(III)-bovine serum albumin complex** | | | | | |
| | $O_2^- + FeTPPS(BSA)^{5-} \rightarrow$ | 9.7 | $5 \times 10^5$ | enz. | C.k. in 0.05 mol L$^{-1}$ borate buffer (in carbonate buffer at pH 10.1); rel. to $k(O_2^- + NDT^{2+}) = 6 \times 10^4$ | 79R111 |
| | | 10.1 | $6 \times 10^5$ | | | |
| 101 | **Ferricyanide ion** | | | | | |
| | $O_2^- + Fe(CN)_6^{3-} \rightarrow O_2 + Fe(CN)_6^{4-}$ | 9.5–9.7 | $(2.7 \pm 0.9) \times 10^2$ (cor. for $I$) | p.r., opt. | P.b.k. at 420–440 nm. | 720431 |
| 102 | **Potassium hexacyanoferrate(III) ion** | | | | | |
| | $O_2^- + KFe(CN)_6^{2-} \rightarrow KFe(CN)_6^{3-} + O_2$ | 9.5–9.7 | $(6.2 \pm 0.6) \times 10^3$ (cor. for $I$) | p.r., opt. | P.b.k. at 420–440 nm. | 720431 |
| 103 | **Hydroxybis(2-pyridinecarboxylato)iron(III)** | | | | | |
| | $HO_2/O_2^- + Fe(2\text{-}pyCO_2)_2OH \rightarrow$ | 8.5 | See comment | p.r., opt. | D.k. at 250 nm in $N_2O/O_2$ (4:1) satd. soln. contg. 0.1 mol L$^{-1}$ formate; $k$(catalytic) $= 9.3 \times 10^4$. | 83A209 |
| 104 | ***N*-Hydroxyethylenediaminetriacetatoferrate(III)** | | | | | |
| | $HO_2/O_2^- + FeHETA \rightarrow$ | 6.0 | $3.8 \times 10^6$ | p.r., opt. | D.k. at 250 nm ($O_2^-$) as well as 280–300 nm ($Fe^{III}$) in $O_2$-satd. soln. contg. 0.02 mol L$^{-1}$ formate ion, $5 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer and $10^{-4}$ mol L$^{-1}$ complex. | 83A158 |
| | | 7.0 | $7.6 \times 10^5$ | | | |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 105 | **Ethylenediaminetetraacetatoferrate(III) ion** | | | | | |
| | $O_2^- + FeEDTA^- \rightarrow$ $FeEDTA^{2-} + O_2$ | | $2 \times 10^6$ | s.f., opt. | P.b.k at 520 nm, data taken above pH 9.5 and compared with earlier data at a variety of ionic strengths and pH to give $k = 2 \times 10^6[H^+]/[H^+] + K_a$ assuming that $FeEDTA(OH)^{3-}$ is unreactive ($pK_a$ for $FeEDTA(H_2O)^{2-} = 7.6$). Velocity increases with ionic strength. At pH 10.4 and $I = 1$ $k \approx 8 \times 10^6$. | 83A163 |
| | | 6.0 | $3.1 \times 10^6$ | p.r., opt. | D.k. at 250 nm ($O_2^-$) as well as 280–300 nm ($Fe^{III}$) in $O_2$-satd. soln. contg. 0.02 mol L$^{-1}$ formate ion, $5 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer and $10^{-4}$ mol L$^{-1}$ complex. | 83A158 |
| | | 7.0 | $1.9 \times 10^6$ | | | |
| | | 8.0 | $5.0 \times 10^5$ | | | |
| | | 5.65 | $(6.2 \pm 1.0) \times 10^6$ | p.r., opt. | D.k. at 310–340 nm in $O_2$-satd. soln. contg. 0.1 mol L$^{-1}$ Na formate and 1–20 $\times 10^{-4}$ mol L$^{-1}$ chelate. | 82A449 |
| | | 6.0 | $(3.6 \pm 0.3) \times 10^6$ | | | |
| | | 6.5 | $(1.8 \pm 0.2) \times 10^6$ | | | |
| | | 6.75 | $(1.5 \pm 0.12) \times 10^6$ | | | |
| | | 7.0 | $(1.3 \pm 0.15) \times 10^6$ | | | |
| | | 7.5 | $(8 \pm 1) \times 10^5$ | | | |
| | | 7.6 | $(7 \pm 0.8) \times 10^5$ | | | |
| | | 7.75 | $(5 \pm 0.05) \times 10^5$ | | | |
| | | 8.0 | $(3 \pm 0.5) \times 10^5$ | | | |
| | | 8.5 | $(2 \pm 0.5) \times 10^5$ | | | |
| | | 9.0 | $<0.1$ | | | |
| | | 9.5 | $<0.1$ | | | |
| | | 10.0 | $<0.1$ | | | |
| | | 8.4 | $1.5 \times 10^5$ | p.r., opt. | D.k. at 250 nm ($O_2^-$) in $O_2$-satd. soln. contg. 0.1 mol L$^{-1}$ EtOH, $1 \times 10^{-4}$ mol L$^{-1}$ EDTA. | 82A446 |
| | | 10.1 | $2 \times 10^5$ | enz., opt. | C.k.; rel. to $k(O_2^- + NBT^{2+}) = 6 \times 10^4$. | 79A018 |
| | | 10.1 | $3 \times 10^5$ | enz., opt. | C.k.; rel. to $k(O_2^- + NBT^{2+}) = 6 \times 10^4$; $k = 4 \times 10^5$ in borate buffer at pH 9.7. | 79R111 |
| | | 5.8 | $5 \times 10^6$ | p.r., opt. | D.k. at 300 nm in $O_2$-satd. soln. contg. $10^{-4}$ mol L$^{-1}$ complex, $10^{-2}$ mol L$^{-1}$ Na formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer at pH 5.8–7.2, $10^{-3}$ mol L$^{-1}$ borax buffer at pH 8.1 and 0.5–1 $\times 10^{-3}$ mol L$^{-1}$ carbonate buffer at pH 9; above the $pK$ at 7.6 the substrate is a hydroxo complex. | 771088 |
| | | 7 | $1.8 \times 10^6$ | | | |
| | | 8.1 | $4.6 \times 10^5$ | | | |
| | | 9 | $\sim 10^5$ | | | |
| 106 | **Diethylenetriaminepentaacetatoferrate(III) ion** | | | | | |
| | $HO_2/O_2^- + FeDTPA^{2-} \rightarrow$ | 6.0 | $<10^4$ | p.r., opt. | D.k. at 250 nm ($O_2^-$) as well as 280–300 nm ($Fe^{III}$) in $O_2$-satd. soln. contg. 0.02 mol L$^{-1}$ formate ion, $5 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer and $10^{-4}$ mol L$^{-1}$ complex. | 83A158 |
| | | 7.0 | $<10^4$ | | | |
| | | 8.0 | $<10^4$ | | | |
| | | 7.0 | $<10^5$ | p.r., opt. | D.k. at 300–320 nm in 0.1 mol L$^{-1}$ Na formate contg. $10^{-1}$ mol L$^{-1}$ phosphate buffer. | 82A449 |
| | $O_2^- + FeDTPA^{2-} \rightarrow$ | 10.1 | $0.8 \times 10^5$ | enz., opt. | C.k.; rel. to $k(O_2^- + NBT^{2+}) = 6 \times 10^4$. | 79A018 |
| 107 | **Adenosine triphosphate-iron(III) complex** | | | | | |
| | $HO_2/O_2^- + Fe^{III}ATP \rightarrow$ | 7.0 | $<10^5$ | p.r., opt. | D.k. at 300–320 nm in 0.1 mol L$^{-1}$ Na formate contg. $10^{-1}$ mol L$^{-1}$ phosphate buffer. | 82A449 |
| 108 | **Desferrioxamine B** | | | | | |
| | $HO_2/O_2^- + DB \rightarrow$ | 7.0 | $<2 \times 10^5$ | p.r., opt. | D.k. at 450–550 nm in 0.1 mol L$^{-1}$ Na formate contg. $10^{-1}$ mol L$^{-1}$ phosphate buffer. | 82A449 |
| 109 | **Hemin** | | | | | |
| | $HO_2/O_2^- + Fe^{3+}$ heme $\rightarrow$ | 9.7 | $\sim 1 \times 10^4$ | enz, opt. | C.k.; rel. to $k(O_2^- + NBT^{2+}) = 6 \times 10^4$, in 0.05 mol L$^{-1}$ borate buffer. Obs. increase in absorbance at 560 nm ($NBT^{2+} \rightarrow$ formazan); $O_2^-$ produced in xanthine/xanthine oxidase system contg. catalase; imidazole complex had similar reactivity. | 79R111 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 110 | **Hemin-diimidazole complex** | | | | | |
| | $O_2^- + Hemin(Im)_2 \rightarrow$ | 9.7 | $\sim 3 \times 10^4$ | | C.k. in soln. contg. 0.05 mol L$^{-1}$ borate buffer; rel. to $k(O_2^- + NBT^{2+}) = 6 \times 10^4$. | 79R111 |
| 111 | **Hydroxyprotoferrihaem dimer** | | | | | |
| | $HO_2/O_2^- +$ $H_2OFe^{III}porOFe^{III}porOH^{n-} \rightarrow$ | 9.2 | $< 1.7 \times 10^3$ | p.r., opt. | No reaction in soln. contg. 0.1 mol L$^{-1}$ formate and $O_2$; $I = 0.1$. Limiting rate. | 761071 |
| 112 | **Hydrogen** | | | | | |
| | $HO_2/O_2^- + H_2 \rightarrow H + H_2O_2$ | $\sim 2$ | $< 1$ | phot. | Data fitting; soln. under 10–100 atm $H_2$. | 767025 |
| 113 | **Hydrogen ion** | | | | | |
| | $O_2^- + H^+ \rightarrow HO_2$ | 4 | $(5 \pm 1) \times 10^{10}$ | p.r., opt. | P.b.k. (and d.k.) at 270 nm in $O_2$-satd. soln. contg. $10^{-4}$ $HClO_4$; protonation reaction. | 761132 |
| | | $\sim 2$ | $7.2 \times 10^{10}$ | phot. | Data fitting. | 767025 |
| | | | $4.8 \times 10^{10}$ | elec., pol. | D.k. | 759347 |
| 114 | **Iodine** | | | | | |
| | $HO_2/O_2^- + I_2 \rightarrow I_2^- + H^+ + O_2$ | 3.9 | $\leqslant 1 \times 10^8$ | p.r., opt. | P.b.k. at 410 nm, in air-satd. soln. contg. 0.4–1 $\times 10^{-4}$ mol L$^{-1}$ $I_2$ and 0.3–2 $\times 10^{-2}$ mol L$^{-1}$ formate ion. | 83A901 |
| | $O_2^- + I_2 \rightarrow I_2^- + O_2$ | 3.9–5.5 | $5.5 \times 10^9$ | p.r., opt. | P.b.k. at 410 nm in air-satd. soln. contg. 0.4–1 $\times 10^{-4}$ mol L$^{-1}$ $I_2$ and 0.3–2 $\times 10^{-2}$ mol L$^{-1}$ formate ion. | 83A901 |
| 115 | **Triiodine ion** | | | | | |
| | $O_2^- + I_3^- \rightarrow I_2^- + I^- + O_2$ | 3.9–5.5 | $8 \times 10^8$ | p.r., opt. | P.b.k. at 700 nm in air-satd. soln. contg. 5 $\times 10^{-3}$ mol L$^{-1}$ $I^-$, 0.4–1 $\times 10^{-4}$ mol L$^{-1}$ $I_2$ and 0.3–2 $\times 10^{-2}$ formate ion. | 83A901 |
| 116 | **Manganese(II) ions** | | | | | |
| | $HO_2/O_2^- + Mn^{2+} \rightarrow MnO_2^+$ | | $(1.1 \pm 0.2) \times 10^8$ | p.r., opt. | P.b.k. at 275 nm in soln. contg. 0.01 mol L$^{-1}$ formate and oxygen; $k = 7.0 \times 10^7$ at $I = 0.5$ ($NaClO_4$) and $3.2 \times 10^7$ in 0.5 mol L$^{-1}$ formate. pH probably 6.7. | 761109 |
| 117 | **Manganese(II) pyrophosphate complex** | | | | | |
| | $HO_2/O_2^- + Mn(II) \rightarrow Mn(III) + H_2O_2$ | 1.1 | $1.31 \times 10^6$ | p.r., opt. | P.b.k. at 260 nm in soln. contg. $10^{-2}$ mol L$^{-1}$ Na pyrophosphate, $10^{-2}$ mol L$^{-1}$ formate, 1.5–5 $\times 10^{-4}$ mol L$^{-1}$ Mn(II); $k$ varies from $3 \times 10^5$ to $4.4 \times 10^7$ with pH 0.14–7.18. | 84A910 |
| | | 6.5 | $2.6 \times 10^7$ | | | |
| | $O_2^- + Mn(II) \rightarrow Mn(III) + H_2O_2$ | 7.3 | $1.3 \times 10^7$ | p.r., opt. | $10^{-4}$ mol L$^{-1}$ $MnSO_4$, $10^{-4}$ mol L$^{-1}$ pyrophosphate, 0.1 mol L$^{-1}$ formate. | 82A455 |
| | | 7.8 | $\sim 6 \times 10^6$ | enz., opt. | P.b.k. at 258 nm; $\epsilon(Mn^{3+}) = 6 \times 10^3$ mol L$^{-1}$ cm$^{-1}$; xanthine-xanthine oxidase system contg. $10^{-5}$ mol L$^{-1}$ $MnCl_2$, $5 \times 10^{-2}$ mol L$^{-1}$ Na pyrophosphate and SOD, assuming $k(O_2^- + SOD) = 2.3 \times 10^9$. | 76R190 |
| 118 | **Manganese(II) sulfate** | | | | | |
| | $HO_2 + MnSO_4 \rightarrow Mn(O_2)SO_4^-$ | 2.7–3.4 | $\sim 6 \times 10^6$ | p.r., opt. | P.b.k. at 230–270 nm in soln. contg. 1–2 $\times 10^{-2}$ mol L$^{-1}$ $Mn^{2+}$, 0.1 mol L$^{-1}$ Na sulfate and 5–20 $\times 10^{-3}$ mol L$^{-1}$ formate. Complex mechanism. | 84A910 |
| | $O_2^- + MnSO_4 \rightarrow Mn(O_2)SO_4^-$ | 5.1–5.6 | $5.2 \times 10^7$ | p.r., opt. | P.b.k. at 270 nm in soln. contg. 1–5 $\times 10^{-3}$ mol L$^{-1}$ $Mn^{2+}$, 0.1 mol L$^{-1}$ Na sulfate and 1–2 $\times 10^{-3}$ mol L$^{-1}$ formate. | 84A910 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 119 | **Manganese(II) formate** | | | | | |
| | $HO_2 + Mn(HCO_2)_2 \rightarrow Mn(O_2)(HCO_2)_2^-$ | 2.2–3.0 | $\sim 6 \times 10^6$ | p.r., opt. | P.b.k. at 260 nm, 3–18 $\times 10^{-3}$ mol L$^{-1}$ $Mn^{2+}$, and 0.4 mol L$^{-1}$ formate. Complex mechanism. | 84A910 |
| | $O_2^- + Mn(HCO_2)_2 \rightarrow Mn(O_2)(HCO_2)_2^-$ | 5.7–7.1 | $4.3 \times 10^7$ | p.r., opt. | P.b.k. at 270 nm in soln. contg. $4.15 \times 10^{-3}$ mol L$^{-1}$ $Mn^{2+}$ and 0.4 mol L$^{-1}$ formate. | 84A910 |
| 120 | **Nitrilotriacetatomanganate(II) ion** | | | | | |
| | $HO_2/O_2^- + MnNTA^- \rightarrow$ | 4.5 | $4.0 \times 10^8$ | p.r., opt. | P.b.k. at 350 and 470 nm. | 78A436 |
| | | 5.5 | $1.2 \times 10^8$ | | | |
| 121 | **Ethylenediaminetetraacetatomanganate(II) ion** | | | | | |
| | $HO_2/O_2^- + MnEDTA^{2-} \rightarrow$ | 4.5 | $3.0 \times 10^7$ | p.r., opt. | P.b.k. at 350 and 475 nm. | 78A436 |
| | | 5.5 | $7.5 \times 10^6$ | | | |
| 122 | **Tetrakis(4-*N*-methylpyridyl)porphinemanganese(III) ion** | | | | | |
| | $O_2^- + MnTMpyP^{5+} \rightarrow$ | 5.6 | $(5.1 \pm 0.5) \times 10^7$ | p.r., opt. | D.k. at 254 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ Na formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer. | 82A319 |
| | | 8.0 | $(4.0 \pm 0.4) \times 10^7$ | | | |
| | | 10.1 | $2.2 \times 10^7$ | enz | Beauchamp-Fridovich assay; rel. to Nitro Blue Tetrazolium conversion to formazan ($NBT^{2+}$ rate not given). | 81R125 |
| 123 | **Tetrakis-4-(*N,N,N*-trimethylammonio)phenylporphinemanganese(III) ion** | | | | | |
| | $HO_2/O_2^- + MnTAPP^{5+} \rightarrow$ | 5.6 | $(1.3 \pm 0.1) \times 10^7$ | p.r., opt. | D.k. at 254 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ Na formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer. | 82A319 |
| | | 8.0 | $(2.9 \pm 0.3) \times 10^6$ | | | |
| | $O_2^- + MnTAPP^{5+} \rightarrow$ | | See comment | | Method not given (enz. or p.r.), $k$(catalytic) $= 3 \times 10^6$; pH not given, reaction in 0.5 mol L$^{-1}$ carbonate buffer. Probably pH 8–10. | 82R172 |
| 124 | **Tetrakis(*p*-sulfonatophenyl)porphinatomanganate(III) ion** | | | | | |
| | $HO_2/O_2^- + MnTPPS^{3-} \rightarrow$ | 5.6 | $\leqslant 6 \times 10^5$ | p.r., opt. | D.k. at 254 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ Na formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer. | 82A319 |
| | | 8.0 | $\leqslant 7 \times 10^4$ | | | |
| 125 | **Ethylenediaminetetraacetatomanganate(III) ion** | | | | | |
| | $O_2^- + MnEDTA^- \rightarrow MnEDTA^{2-} + O_2$ | 10.0 | $\sim (5 \pm 1) \times 10^4$ | $KO_2$, s.f., opt. | D.k. at 500 nm ($Mn^{III}$); soln. contains $KMn^{III}EDTA$ which is probably a hydroxo species. | 79A329 |
| 126 | **1,2-Cyclohexanediaminetetraacetatomanganate(III) ion** | | | | | |
| | $HO_2/O_2^- + MnCyDTA^- \rightarrow O_2 + MnCyDTA^{2-}$ | | $\sim 1 \times 10^6$ | $KO_2$, opt., s.f. | D.k. at 500 nm; pH not given explicitly. | 79A329 |
| 127 | **Permanganate ion** | | | | | |
| | $HO_2/O_2^- + MnO_4^- \rightarrow H^+ + MnO_4^{2-} + O_2$ | 2 | $8 \times 10^6$ | p.r., opt. | D.k. | 650385 |
| 128 | **Octacyanomolybdate(IV) ion** | | | | | |
| | $HO_2/O_2^- + Mo(CN)_8^{4-} \rightarrow Mo(CN)_8^{3-} + H_2O_2$ | 2.0 | $(5.7 \pm 0.6) \times 10^4$ | p.r., opt. | P.b.k. at 385 nm in soln. contg. 0.3 mol L$^{-1}$ formate and $HClO_4$ and $O_2$. | 761140 |
| 129 | **Octacyanomolybdate(V) ion** | | | | | |
| | $O_2^- + Mo(CN)_8^{3-} \rightarrow Mo(CN)_8^{4-} + O_2$ | 8.3–10.4 | $(3.0 \pm 0.3) \times 10^5$ | p.r., opt. | D.k. at 385 nm in soln. contg. $O_2$ and Mo(IV), Mo(V), and $5 \times 10^{-3}$ mol L$^{-1}$ $NaClO_4$. | 761140 |
| 130 | **Azide radical** | | | | | |
| | $O_2^- + \cdot N_3 \rightarrow N_3^- + O_2$ | | $(1.2 \pm 0.2) \times 10^{10}$ | p.r., opt. | D.k. in $O_2$-satd. soln at 278 nm; cor. for $k(\cdot N_3 + \cdot N_3)$; pH not given explicitly, probably 8.5–10.8. | 81A216 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 131 | **Hydroxylamine, p$K_a$ = 6** | | | | | |
| | $HO_2 + NH_2OH_2^+/NH_2OH \rightarrow$ | 1.1–10.5 | <44 | p.r., s.f., opt. | D.k. at 250–270 nm in soln. contg. 0.01–0.2 mol L$^{-1}$ $NH_2OH$, 0.001–1 mol L$^{-1}$ formate and EDTA; studied as a function of pH. See paper for limiting rates at all pH. Authors feel there is negligible reaction. | 84A908 |
| | $O_2^- + NH_2OH_2^+/NH_2OH \rightarrow$ | 1.1–10.5 | <35 | p.r., s.f., opt. | D.k. at 250–270 nm, 0.01–0.2 mol L$^{-1}$ $NH_2OH$, 0.001–1 mol L$^{-1}$ formate, EDTA; studied as a function of pH. See paper for limiting rates at all pH. Authors feel there is negligible reaction. | 84A908 |
| 132 | **Nitrogen dioxide** | | | | | |
| | $HO_2 + NO_2 \rightarrow HO_2NO_2$ | 1.85 | $4 \times 10^9$ | p.r., opt. | Deduced from p.b.k. at 350 nm and d.k. of transient (nitroform) in soln. contg. oxygen, formic acid and tetranitromethane; reverse reaction is interpreted to have $k$ = 0.014 ± 0.002 s$^{-1}$. | 750347 |
| 133 | **Nitrite ion** | | | | | |
| | $HO_2/O_2^- + NO_2^- \rightarrow NO_2^{2-} + O_2$ | | $5 \times 10^6$ | γ-r. | Obs. $G(NF^-)$ in soln. contg. tetranitromethane. | 750403 |
| 134 | **5,7,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecanenickel(II) ion** | | | | | |
| | $HO_2 + Ni(aneN_4)^{2+} \rightarrow H^+ + O_2 + Ni(aneN_4)^{3+}$ | 0.3 | $(1.1 \pm 0.2) \times 10^7$ | p.r., opt. | P.b.k. in soln. contg. $H_2O_2$ and 0.5 mol L$^{-1}$ acid; acid catalyzed. | 79A038 |
| 135 | **Tetrakis(4-*N*-methylpyridyl)porphinenickel(II) ion** | | | | | |
| | $HO_2/O_2^- + NiTMpyP^{4+} \rightarrow$ | 5.6 | $\leqslant 6 \times 10^5$ | p.r., opt. | D.k. at 254 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ Na formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer. | 82A319 |
| | | 8.0 | $\leqslant 8 \times 10^4$ | | | |
| 136 | **Tetrakis-4-(*N,N,N*-trimethylammonio)phenylporphinenickel(II) ion** | | | | | |
| | $HO_2/O_2^- + NiTAPP^{4+} \rightarrow$ | 5.6 | $\leqslant 8 \times 10^5$ | p.r., opt. | D.k. at 254 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ Na formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer. | 82A319 |
| | | 8.0 | $\leqslant 7 \times 10^4$ | | | |
| 137 | **Tetrakis(*p*-sulfonatophenyl)porphinatonickelate(II) ion** | | | | | |
| | $HO_2/O_2^- + NiTPPS^{4-} \rightarrow$ | 5.6 | $\leqslant 6 \times 10^5$ | p.r., opt. | D.k. at 254 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ Na formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer. | 82A319 |
| | | 8.0 | $\leqslant 7 \times 10^4$ | | | |
| 138 | **5,7,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecanenickel(III) ion** | | | | | |
| | $HO_2/O_2^- + Ni(aneN_4)^{3+} \rightarrow Ni(aneN_4)^{2+} + O_2$ | 2.0 | $(1.0 \pm 0.2) \times 10^5$ | p.r., opt. | D.k. | 79A038 |
| | $O_2^- + Ni(aneN_4)^{3+} \rightarrow Ni(aneN_4)^{2+} + O_2$ | 6.2 | $(2.1 \pm 0.4) \times 10^9$ | p.r., opt. | D.k. | 79A038 |
| 139 | **5,7,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(III) ion** | | | | | |
| | $HO_2/O_2^- + Ni(4,11\text{-dieneN}_4)^{3+} \rightarrow Ni(4,11\text{-dieneN}_4)^{2+} + O_2$ | 2.0 | $(1.6 \pm 0.3) \times 10^5$ | p.r., opt. | D.k. | 79A038 |
| | $O_2^- + Ni(4,11\text{-dieneN}_4)^{3+} \rightarrow Ni(4,11\text{-dieneN}_4)^{2+} + O_2$ | 6.2 | $(1.6 \pm 0.4) \times 10^9$ | p.r., opt. | D.k. | 79A038 |
| 140 | **5,7,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraenenickel(III) ion** | | | | | |
| | $HO_2/O_2^- + Ni(1,4,8,11\text{-tetraeneN}_4)^{3+} \rightarrow O_2 + Ni(1,4,8,11\text{-tetraeneN}_4)^{2+}$ | 2.0 | $(8.5 \pm 1.0) \times 10^5$ | p.r., opt. | D.k. | 79A038 |
| | $O_2^- + Ni(1,4,8,11\text{-tetraeneN}_4)^{3+} \rightarrow O_2 + Ni(1,4,8,11\text{-tetraeneN}_4)^{2+}$ | 6.2 | $(1.0 \pm 0.2) \times 10^9$ | p.r., opt. | D.k. | 79A038 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 141 | **Hydroxyl** | | | | | |
| | $HO_2 + OH \rightarrow H_2O_3$ | 0.46–6.76 | $0.71 \times 10^{10}$ | p.r., opt. | Calcd. from $G$ values for oxygenated aqueous $H_2O_2$ with sulfuric and perchloric acid; product detn. in [630075]. | 680014 |
| | $O_2^- + OH \rightarrow OH^- + O_2$ | 0.46–6.76 | $1.01 \times 10^{10}$ | p.r., opt. | Calcd. from $G$ values for oxygenated aqueous $H_2O_2$ with sulfuric and perchloric acid. | 680014 |
| 142 | **Oxygen ion(1−)** | | | | | |
| | $O_2^- + O^- \rightarrow OH^- + OH^- + O_2$ | 13–14 | $(6.0 \pm 1.0) \times 10^8$ | p.r., opt. | D.k. at 430 nm ($O_3^-$) as well simultaneous buildup at 250 nm ($O_2^-$) and decay, in soln. satd. with 4 MPa $N_2O$ and 0–1 MPa $O_2$; computer simulation. | 82A133 |
| 143 | **Hydrogen peroxide** | | | | | |
| | $HO_2 + H_2O_2 \rightarrow OH + H_2O + O_2$ | 0.5–3.5 | $0.50 \pm 0.09$ | γ-r., chem. | Obs. oxygen yield in 0.08–1.5 mol L$^{-1}$ $H_2O_2$ soln.; pH independent rate. | 79A001 |
| | | 2.3 | $3.0 \pm 0.6$ | γ-r., chem. | Calcd. from obs. decrease in $[H_2O_2]$ under 2 atm $N_2$ or $O_2$. | 78A362 |
| | | ~2 | <5 | phot. | Data fitting; soln. under 10–100 atm. $H_2$. | 767025 |
| | | 0.8–1.5 | $0.20 \pm 0.01$ | γ-r., chem. | C.k.; obs. $G(-H_2O_2)$; includes $k(H_2O_2 + H_2O_2 \rightarrow H_3O^+ + O_2 + OH)$; rel. to $k(HO_2 + HO_2) = 1.1 \times 10^6$. | 690643 |
| | | 1 | $1 \times 10^{-2}$ | γ-r., chem. | Mechanistic fit; $k$ at 10°C; $[H_2O_2] \sim$ 1–35 mol L$^{-1}$. | 650046 |
| | $HO_2/O_2^- + H_2O_2 \rightarrow OH + H_2O + O_2$ | nat. | 1.1 | γ-r., chem. | $k$ at 0°C. no pH effects considered. | 530014 |
| | | nat. | $3.7 \pm 1.6$ | phot., chem. | Propagation step in chain reaction; $k$ at 25°C; no pH effects considered. | 530014 |
| | $O_2^- + H_2O_2 \rightarrow OH^- + OH + O_2$ | 7.0–9.9 | $0.13 \pm 0.07$ | γ-r., chem. | Obs. $O_2$ yield as function of $[H_2O_2]$ in soln. contg. 0.08–1.5 mol L$^{-1}$ $H_2O_2$; assumed values of radical combination rates and p$K$; pH independent rate. | 79A001 |
| | | 5.4–7.85 | $2.25 \pm 0.20$ | γ-r., chem. | Obs. $G(-H_2O_2)$ vs dose rate or $[H_2O_2]$. | 78A364 |
| | | 9.6 | $<0.23 \pm 0.09$ | γ-r. | Anal. for hydroxylated products in soln. contg. $5 \times 10^{-4}$ mol L$^{-1}$ benzoate and $H_2O_2$. | 78A389 |
| | | 5.4–9.4 | $<10^{-4}$ | $KO_2$ | No redn. of $7 \times 10^{-3}$ mol L$^{-1}$ $p$-nitrosodimethylaniline obs. (by OH formed in reaction). Limiting value. | 779154 |
| 144 | **Hydroperoxide ion** | | | | | |
| | $O_2^- + HO_2^- \rightarrow H_2O_2 + O_2$ | 8.9–12.7 | <2 | $KO_2$, opt. | D.k at ~250 nm. | 769352 |
| 145 | **Ozone** | | | | | |
| | $O_2^- + O_3 \rightarrow O_3^- + O_2$ | 8.4–10.3 | $(1.52 \pm 0.05) \times 10^9$ | p.r., opt. | P.b.k. at 430 nm in soln. contg. 0.025–0.1 mol L$^{-1}$ $HCO_3^-/CO_3^{2-}$ and $(0.41–1.71) \times 10^{-4}$ mol L$^{-1}$ ozone. | 83A117 |
| 146 | **Osmium tetroxide** | | | | | |
| | $HO_2 + OsO_4 \rightarrow H^+ + O_2 + OsO_4^-$ | <1 | $5.7 \times 10^5$ | γ-r., chem. | C.k.; obs. $G(H_2O_2)$; dose rate $9.7 \times 10^{18}$ eV cm$^{-3}$h$^{-1}$; rel. to $k(HO_2 + HO_2) = 2.35 \times 10^6$. | 640050 |
| 147 | **Pentaammine(isonicotinamide)ruthenium(II) ion** | | | | | |
| | $HO_2/O_2^- + Ru(NH_3)_5isn^{2+} \rightarrow HO_2^- + Ru(NH_3)_5isn^{3+}$ | 2.35 | $(9.07 \pm 0.54) \times 10^6$ | p.r., opt. | P.b.k. in soln. contg. 0.1 mol L$^{-1}$ formic acid, $k$ for third-order $H^+$ catalyzed reaction $<5.7 \times 10^6$ L$^2$ mol$^{-2}$ s$^{-1}$. | 80A317 |
| 148 | **Pentaammine(isonicotinamide)ruthenium(III) ion** | | | | | |
| | $HO_2 + Ru(NH_3)_5isn^{3+} \rightarrow H^+ + Ru(NH_3)_5isn^{2+} + O_2$ | 3.3–4.9 | $<2.0 \times 10^6$ | p.r., opt. | P.b.k.; $I = 0.1$. | 80A317 |
| | $O_2^- + Ru(NH_3)_5isn^{3+} \rightarrow Ru(NH_3)_5isn^{2+} + O_2$ | 3.86–4.91 | $(2.18 \pm 0.19) \times 10^8$ | p.r., opt. | P.b.k. in $O_2$-satd. soln. contg. formate; $I =$ 0.1 | 80A317 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 149 | **Tris(2,2'-bipyridine)ruthenium(III) ion** | | | | | |
| | $HO_2 + Ru(bpy)_3^{3+} \rightarrow H^+ + Ru(bpy)_3^{2+} + O_2$ | ~1 | $(1.25 \pm 0.1) \times 10^7$ | f.p., opt. | D.k. at 450 nm in air-satd. soln. contg. 0.5 mol L$^{-1}$ $H_2SO_4$. | 82A198 |
| 150 | **Sulfide ion** | | | | | |
| | $HO_2/O_2^- + S^{2-} \rightarrow$ | 7.8 | $1.5 \times 10^6$ | enz., opt. | Xanthine-xanthine oxidase system; c.k., rel. to $k(HO_2/O_2^- + \text{adrenaline}) = 4 \times 10^4$. | 76R183 |
| 151 | **Sulfite ion** | | | | | |
| | $HO_2/O_2^- + SO_3^{2-} \rightarrow SO_3^- + OH^- + H_2O_2$ | 9.8 | 82 | p.r., opt. | D.k. at 245 nm in aerated soln. contg. $3 \times 10^{-3}$ mol L$^{-1}$ sulfite ion and 0.3 mol L$^{-1}$ formate ion; data fitting with $2k(O_2^- + O_2^-) = 2500$ and $\epsilon(O_2^-) = 2000$ L mol$^{-1}$ cm$^{-1}$. | 81G067 |
| 152 | **Thiocyanogen** | | | | | |
| | $HO_2 + SCN \rightarrow H^+ + SCN^- + O_2$ | 1 | $1.6 \times 10^9$ | p.r., opt. | C.k.; pH effect on decay $SCN + SCN \rightarrow (SCN)_2$. | 650386 |
| 153 | **Tellurate(IV) ion** | | | | | |
| | $HO_2 + TeO_3^{2-} \rightarrow TeO_3 + OH$ | 0.4 | $1.9 \times 10^2$ | $\gamma$-r., chem. | C.k.; more than one rate involved in calcn.; rel. to $k(HO_2 + HO_2) = 2.5 \times 10^6$. | 680356 |
| 154 | **Thorium(IV) ion** | | | | | |
| | $HO_2 + Th^{4+} \rightarrow$ Th(IV)-$HO_2$ | 1 | $(1.8 \pm 0.2) \times 10^6$ | p.r., opt. | P.b.k. | 741107 |
| | | ~1 | $\geqslant 5 \times 10^6$ | esr | D.k. as well as p.b.k.; radical from Ce(IV)-$H_2O_2$. | 739071 |
| 155 | **Thorium(IV)-hydroperoxy complex** | | | | | |
| | Th(IV)-$HO_2 \rightarrow Th^{4+} + H_2O_2 + O_2$ | 1 | $(8.0 \pm 2.0) \times 10^5$ | esr | Radical from Ce(IV)-$H_2O_2$; $k(\text{Th(IV)-}HO_2 \rightarrow \text{Th(IV)} + H_2O_2 + O_2) = (5 \pm 2) \times 10^2$. | 739071 |
| 156 | **Thallium(II) ion** | | | | | |
| | $HO_2 + Tl^{2+} \rightarrow H^+ + Tl^+ + O_2$ | 1 | $(2.5 \pm 1) \times 10^9$ | p.r., opt. | D.k. ($Tl^{2+}$); rel. to $k(Tl^{2+} + Tl^{2+}) = 2.3 \times 10^9$. | 660097 |
| 157 | **Uranyl(VI) ion** | | | | | |
| | $HO_2 + UO_2^{2+} \rightarrow$ $UO_2$-$HO_2^{2+}$ | 1 | $(1.5 \pm 0.1) \times 10^5$ | p.r., opt. | P.b.k. and d.k. | 741107 |
| | | ~1 | $\geqslant 1 \times 10^5$ | esr | D.k. as well as p.b.k.; radical from Ce(IV)-$H_2O_2$. | 739071 |
| 158 | **Dioxouranium(VI)-hydroperoxy complex** | | | | | |
| | $HO_2 +$ $UO_2$-$HO_2^{2+} \rightarrow UO_2^{2+} + H_2O_2 + O_2$ | | $(5 \pm 1) \times 10^5$ | p.r., opt. | P.b.k. and d.k.; $k(UO_2^{2+}\text{-}HO_2 \rightarrow UO_2^{2+} + H_2O_2 + O_2) = (8 \pm 2) \times 10^4$. | 741107 |
| | | ~1 | $(9.0 \pm 1.5) \times 10^5$ | esr. | P.b.k. as well as d.k. | 739071 |
| 159 | **Oxoperoxyvanadium(IV) ion** | | | | | |
| | $HO_2/O_2^- + VO(O_2)^+ \rightarrow$ | | $(9.4 \pm 1) \times 10^4$ | esr | Radical from Ce(IV)-$H_2O_2$; flow technique; 0.1 mol L$^{-1}$ $HClO_4$ soln.; rel. to $k(HO_2 + HO_2) = 9 \times 10^5$. | 709058 |
| 160 | **Tetrakis(4-*N*-methylpyridyl)porphinatezinc(II) ion** | | | | | |
| | $HO_2/O_2^- + ZnTMpyP^{4+} \rightarrow$ | 5.6 | $\leqslant 8 \times 10^5$ | p.r., opt. | D.k. at 254 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ Na formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer. | 82A319 |
| | | 8.0 | $\leqslant 7 \times 10^4$ | | | |
| | $O_2^- + ZnTMpyP^{4+} \rightarrow$ | | See comment | | Method not given (enz. or p.r.), $k$(catalytic) $\leqslant 10^5$; pH not given, reaction in 0.5 mol L$^{-1}$ carbonate buffer. | 82R172 |
| 161 | **Tetrakis-4-(*N,N,N*-trimethylammonio)phenylporphinezinc(II) ion** | | | | | |
| | $HO_2/O_2^- + ZnTAPP^{4+} \rightarrow$ | 5.6 | $\leqslant 8 \times 10^5$ | p.r., opt. | D.k. at 254 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ Na formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer. | 82A319 |
| | | 8.0 | $\leqslant 1 \times 10^5$ | | | |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 162 | **Tetrakis(*p*-sulfonatophenyl)porphinatozincate(II) ion** | | | | | |
| | $HO_2/O_2^- + ZnTPPS^{4-} \rightarrow$ | 5.6 | $\leqslant 6 \times 10^5$ | p.r., opt. | D.k. at 254 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ Na formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate buffer. | 82A319 |
| | | 8.0 | $\leqslant 7 \times 10^4$ | | | |
| 163 | **Bis(2-pyridinecarboxylato)zinc(II)** | | | | | |
| | $HO_2/O_2^- + Zn(2\text{-}pyCO_2)_2 \rightarrow$ | | | p.r., opt. | D.k. at 250 nm in $N_2O/O_2$ (4:1) satd. soln. contg. 0.1 mol L$^{-1}$ formate; pH not given, probably 8.5; no reaction obs. | 83A209 |
| 164 | **Acetate ion** | | | | | |
| | $O_2^- + CH_3CO_2^- \rightarrow$ | 10.1 | $<0.06$ | *e*-r., s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and $10^{-4}$ mol L$^{-1}$ EDTA and 0.01–0.1 mol L$^{-1}$ acetate; no reaction. | 770046 |
| 165 | **2-Acetylaminofluorene** | | | | | |
| | $HO_2/O_2^- +$ $C_{13}H_9NHCOCH_3 \rightarrow$ | | $\sim 3.5 \times 10^7$ | p.r. | C.k. in soln. contg. 0.01 mol L$^{-1}$ CTAB; rel. to $k(O_2^- + Q) = 9.5 \times 10^8$. pH not given. | 78A367 |
| 166 | **Acetyl peroxide** | | | | | |
| | $HO_2/O_2^- + (CH_3CO)_2O_2 \rightarrow$ | | $2 \times 10^7$ | p.r., opt. | C.k. with benzoquinone; pH not given. | 81A374 |
| 167 | **Adrenaline** | | | | | |
| | $HO_2/O_2^- + Adr \rightarrow$ $AdrO\cdot + H_3O_+$ | 7.8 | $5.4 \times 10^4$ | enz., opt. | P.b.k. at 485 nm (buildup of adrenochrome); xanthine-xanthine oxidase system, no buffers. | 78A483 |
| | | 9.5 | $2.5 \times 10^4$ | | | |
| | | 7.8 | $4.0 \times 10^4$ | enz., opt. | Xanthine-xanthine oxidase system; c.k. with Cu,Zn-SOD from spinach, $k(O_2^- + SOD) = 2.3 \times 10^9$. | 76R183 |
| 168 | **Adrenalone** | | | | | |
| | $HO_2/O_2^- + Adr \rightarrow AdrO\cdot$ | 7.0 | $(2.34 \pm 0.31) \times 10^7$ | p.r. | C.k.; rel. to $k(O_2^- + DCIP) = 2.14 \times 10^8$. | 79A240 |
| 169 | **DL-Alanine, p$K_a$ = 2.3, 9.8** | | | | | |
| | $HO_2 + Ala \rightarrow$ | 1.6 | $<44 \pm 11.0$ | $\gamma$-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ alanine; upper limit. | 79A358 |
| | $O_2^- + Ala \rightarrow$ | 10.0 | $<0.06 \pm 0.02$ | $\gamma$-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ alanine, no reaction. | 79A358 |
| 170 | **Alloxan** | | | | | |
| | $HO_2/O_2^- + Al \rightarrow O_2 + \cdot AlH$ | 5.7 | $(5 \pm 1) \times 10^5$ | p.r., opt. | Buildup and decay of dialuric acid (275 nm) and semiquinone at 310 and 370 nm in soln contg. 0.1 mol L$^{-1}$ formate ion, $1.46 \times 10^{-4}$ mol L$^{-1}$ $O_2$, $5 \times 10^{-3}$ mol L$^{-1}$ alloxan; assumed mechanism, $\epsilon(\cdot AlH) =$ 4000(275), 4900(310) and 1900(370 nm), $\epsilon(Al) =$ 16000(275) and 160(310 nm). | 81A271 |
| 171 | **Alloxan semiquinone** | | | | | |
| | $HO_2/O_2^- + \cdot AlH \rightarrow Al + H_2O_2$ | 5.7 | $(2.5 \pm 0.5) \times 10^8$ | p.r., opt. | Buildup and decay of dialuric acid (275 nm) and semiquinone at 310 and 370 nm in soln contg. 0.1 mol L$^{-1}$ formate ion, $1.46 \times 10^{-4}$ mol L$^{-1}$ $O_2$, $5 \times 10^{-3}$ mol L$^{-1}$ alloxan; assumed mechanism, $\epsilon(\cdot AlH) =$ 4000(275), 4900(310) and 1900(370 nm), $\epsilon(Al) =$ 16000(275) and 160(310 nm). | 81A271 |
| 172 | **Arachidonate ion** | | | | | |
| | $O_2^- + A^- \rightarrow$ | alk. | $10^{-2}$–$10^{-1}$ | s.f., opt. | Anaerobic conditions; 85% v/v EtOH in 0.001–0.01 mol L$^{-1}$ KOH/$H_2O$. D.k. at 240–270 nm. Reaction negligible. | 83A087 |
| | | 11.0 | $<1$ | p.r., opt. | D.k. in soln. contg. 0.6 mol L$^{-1}$ formate, 0.01 mol L$^{-1}$ arachidonate. | 78A365 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 173 | **Arachidonic acid** | | | | | |
| | $HO_2 + AH \rightarrow$ | acid | $(3.05 \pm 0.29) \times 10^3$ | s.f., opt. | 85% v/v ethanolic soln.; d.k. at 240–270 nm; 0.05 mol L$^{-1}$ $H_2SO_4$. | 83A087 |
| 174 | **L-Arginine, p$K_a$ = 1.82, 9, 12.5** | | | | | |
| | $HO_2 + Arg \rightarrow$ | 1.6 | $<63.0 \pm 14.0$ | γ-r., s.f., opt. | D.k. in $O_2$—satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ arginine; upper limit. | 79A358 |
| | $O_2^- + Arg \rightarrow$ | 10.1 | $<0.13 \pm 0.03$ | γ-r., s.f., opt. | D.k. in $O_2$–satd. soln. contg. formate and $5\times10^{-5}$ mol L$^{-1}$ EDTA and 0.15 mol L$^{-1}$ arginine; no reaction. | 79A358 |
| 175 | **Ascorbate oxidase** | | | | | |
| | $HO_2/O_2^- + AAO \rightarrow$ | 7.5 | | p.r., opt. | D.k. at 250 and 610 nm in oxygenated soln. contg. $2 \times 10^{-6}$ mol L$^{-1}$ AAO and 0.1 mol L$^{-1}$ formate ion; no bleaching at 610 nm; no reaction obs. | 83A147 |
| 176 | **Ascorbate radical anion** | | | | | |
| | $HO_2 + \cdot A^- \rightarrow HO_2^- + A$ | 1.42–2.72 | $(5.0 \pm 0.5) \times 10^9$ | p.r., opt. | D.k. at 360 nm ($A\cdot^-$) in $O_2$-satd. soln. contg. (0.1 1) $\times 10^{-3}$ mol L$^{-1}$ $AH_2$. | 83A103 |
| | $O_2^- + \cdot A^- \rightarrow OH^- + HO_2^- + A$ | 7.8, 8.0 | $(2.6 \pm 0.4) \times 10^8$ | p.r., opt. | D.k. at 360 nm ($A\cdot^-$) in $O_2$-satd. soln. contg. (0.1–1) $\times 10^{-3}$ mol L$^{-1}$ $AH_2$. | 83A103 |
| | | 7.4 | $<2.3 \times 10^8$ | chem., opt. | Estd. from $k(AH^- + O_2^-)[AH^-]/k(\cdot A^- + O_2^-)[\cdot AH] = 22$ s$^{-1}$ detd. in soln. contg. ascorbate, catalase, $FeEDTA^-$ and SOD, followed at 265 nm. | 83R034 |
| 177 | **Ascorbic acid, p$K_a$ = 4.1** | | | | | |
| | $HO_2 + AH_2 \rightarrow \cdot A^- + H_2O_2$ | 0.3–1.0 | $1.6 \times 10^4$ | s.f., opt. | D.k. in soln. contg. 0.1 mol L$^{-1}$ formate ion. | 83A103 |
| | $HO_2 + AH^- \rightarrow \cdot A^- + H_2O_2$ | 3–8 | | s.f., opt. | Fitting process gave $k + 0.356k(O_2^- + AH_2) = 1.22 \times 10^7$. | 83A103 |
| | $HO_2/O_2^- + AH_2/AH^- \rightarrow \cdot A^- + H_2O_2$ | ~3 | $(1.25 \pm 0.15) \times 10^6$ | f.p., opt. | P.b.k. at 360 nm; cor. for $\cdot A^-$ decay; detd. from pH dependence (3–8); $I = 0.02$. | 79A340 |
| | $HO_2/O_2^- + AH_2/AH^- \rightarrow \cdot A^- + H_2O_2$ | 7.4 | $2.7 \times 10^5$ | enz., opt. | D.k. at 249.6 nm in soln. contg. 0.1 mol L$^{-1}$ phosphate buffer and xanthine-xanthine oxidase. Observed rate. Rel. to $k(O_2^- + SOD) = 1.9 \times 10^9$. | 751031 |
| | $O_2^- + AH^- \rightarrow HO_2^- + \cdot A^-$ | 3–8 | $(5.75 \pm 0.35) \times 10^4$ | f.p., opt. | P.b.k. at 360 nm; cor. for $\cdot A^-$ decay; detd. from pH dependence (3–8); $I = 0.02$. | 79A340 |
| | | 9.9 | $(1.52 \pm 0.1) \times 10^5$ | s.f., opt. | D.k. at 270 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and $2 \times 10^{-4}$ mol L$^{-1}$ EDTA; cor. for $O_2^-$ decay. Factor of 2 should be considered to recalculate rate. | 770046 |
| | $O_2^- + AH^- \rightarrow$ unidentified product | 8.2–11.0 | $5 \times 10^4$ | s.f., opt. | D.k. in soln. contg. 0.1 mol L$^{-1}$ formate ion. Rate taken from pH vs $k_{obs}$ study. Products not determined. | 83A103 |
| 178 | **DL-Asparagine, p$K_a$ = 2.213, 8.85** | | | | | |
| | $HO_2 + Asn \rightarrow$ | 1.4 | $<53.8 \pm 10.0$ | γ-r., s.f., opt. | D.k. in $O_2$-satd. formate soln. contg. $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ asparagine; upper limit. | 79A358 |
| | $O_2^- + Asn \rightarrow$ | 10.1 | $<0.16 \pm 0.02$ | γ-r., s.f., opt. | D.k. in $O_2$-satd. formate soln. contg. $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ asparagine; no reaction. | 79A358 |
| 179 | **DL-Aspartic acid, p$K_a$ = 2.1, 4.0, 9.82** | | | | | |
| | $HO_2 + Asp \rightarrow$ | 1.5 | $<12.0 \pm 4.0$ | γ-r., s.f., opt. | D.k. in $O_2$—satd. formate soln. contg. $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ aspartic acid; upper limit. | 79A358 |
| | $O_2^- + Asp \rightarrow$ | 10.0 | $<0.18 \pm 0.04$ | γ-r., s.f., opt. | D.k. in $O_2$–satd. formate soln. contg. $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ aspartic acid; no reaction. | 79A358 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 180 | **Benzidine** | | | | | |
| | $HO_2/O_2^- + H_2NC_6H_4C_6H_4NH_2 \rightarrow$ | | $>25 \times 10^7$ | p.r. | C.k.; rel. to $k(O_2^- + Q) = 9.5 \times 10^8$; pH not given | 78A367 |
| 181 | **Benzo[*a*]pyrene** | | | | | |
| | $HO_2/O_2^- + C_{20}H_{12} \rightarrow$ | | $<1 \times 10^7$ | p.r. | C.k.; rel. to $k(O_2^- + Q) = 9.5 \times 10^8$; pH not given. | 78A367 |
| 182 | **1,4-Benzoquinone** | | | | | |
| | $O_2^- + Q \rightarrow Q^{\cdot -} + O_2$ | ~7 | $(9 \pm 1) \times 10^8$ | p.r., opt. | P.b.k. at 410 nm in $O_2$-satd. soln. contg. 0.5 mol L$^{-1}$ *tert*-BuOH. | 761056 |
| | | 6.9 | $9.0 \times 10^8$ (±10%) | p.r., opt. | P.b.k. at 430 nm in soln. contg. 0.1 mol L$^{-1}$ formate, $2 \times 10^{-5}$ mol L$^{-1}$ Q and $7 \times 10^{-4}$ mol L$^{-1}$ $O_2$. | 730049 |
| | | 7.0 | $9.8 \times 10^8$ | p.r., opt. | P.b.k. at 430 nm in soln. contg. $5 \times 10^{-5}$ mol L$^{-1}$ Q. | 730068 |
| | | ~7 | $9.6 \times 10^8$ | p.r., opt. | P.b.k. at 430 nm in $O_2$—satd. soln. contg. $10^{-4}$ mol L$^{-1}$ Q and 1.0 mol L$^{-1}$ *tert*-BuOH. | 710619 |
| 183 | **Bilirubin** | | | | | |
| | $HO_2/O_2^- + C_{33}H_{36}N_4O_6 \rightarrow$ | 8.3 | $2.3 \times 10^4$ | enz., opt. | D.k. at 446 nm; xanthine-xanthine oxidase system. | 82R164 |
| 184 | **Biliverdin** | | | | | |
| | $HO_2/O_2^- + C_{33}H_{34}N_4O_6 \rightarrow$ | 8.3 | $7 \times 10^3$ | enz., opt. | D.k. at 377 or 650 nm; xanthine-xanthine oxidase system. | 82R164 |
| 185 | **1,1'-Bis(2-hydroxyethyl)-4,4'-bipyridinium radical ion(1+)** | | | | | |
| | $O_2^- + BP^{\cdot +} \rightarrow$ | 6.8 | $(12.0 \pm 1) \times 10^8$ | p.r. | Ar-satd. soln. contg. $10^{-3}$ mol L$^{-1}$ $BP^{2+}$ $2Cl^-$, 0.1 mol L$^{-1}$ Na formate and ~0.3% $O_2$. | 78A321 |
| 186 | ***N*-Bromo-2,2,6,6-tetramethylpiperidine** | | | | | |
| | $HO_2/O_2^- + (CH_3)_4C_5H_6NBr \rightarrow Br^- + (CH_3)_4C_5H_6N\cdot + O_2$ | 9.2 | $1.1 \times 10^3$ | $KO_2$, esr | Estd. from formn of nitroxide radical by subsequent reaction. DMSO/$H_2O$ system contg. 18-crown-6. | 79A184 |
| 187 | ***tert*-Butyl allyl peroxide** | | | | | |
| | $O_2^- + ROOR' \rightarrow$ | | | s.f., opt. | D.k. at 250–270 nm in 80% EtOH soln. with $10^{-2}$ mol L$^{-1}$ KOH, $1 \times 10^{-5}$ mol L$^{-1}$ EDTA, $1.2 \times 10^{-3}$ mol L$^{-1}$ $O_2$; peroxide concn. $3 \times 10^{-3}$ mol L$^{-1}$; no reaction obs. | 84A909 |
| | $HO_2 + ROOR' \rightarrow$ | | | s.f., opt. | D.k. at 250–270 nm in 80% EtOH soln. with $5 \times 10^{-2}$ mol L$^{-1}$ $H_2SO_4$, $1 \times 10^{-5}$ mol L$^{-1}$ EDTA, $1.2 \times 10^{-3}$ mol L$^{-1}$ $O_2$; peroxide concn. $3.8 \times 10^{-2}$ mol L$^{-1}$; no reaction obs. | 84A909 |
| 188 | ***tert*-Butylhydroquinone** | | | | | |
| | $HO_2 + (CH_3)_3CC_6H_3$-1,4-$(OH)_2 \rightarrow$ | 0.5–1.0 | $1.2 \times 10^4$ | s.f., opt. | D.k. at 240–250 nm in soln. contg. $10^{-2}$ mol L$^{-1}$ formate, EDTA, and substrate from $10^{-4}$–$2 \times 10^{-3}$ mol L$^{-1}$. | 83A902 |
| | $O_2^- + (CH_3)_3CC_6H_3$-1,4-$(OH)_2 \rightarrow$ | 5.0–7.0 | $5 \times 10^4$ | s.f., opt. | D.k. at 240–250 nm in soln. contg. $10^{-2}$ mol L$^{-1}$ formate, EDTA, and substrate from $10^{-4}$–$2 \times 10^{-3}$ mol L$^{-1}$. | 83A902 |
| 189 | **Catechol** | | | | | |
| | $HO_2 + 1,2\text{-}C_6H_4(OH)_2 \rightarrow$ | 0.5–9 | $(4.7 \pm 0.5) \times 10^4$ | s.f., opt. | D.k. at 245 nm; soln. prepd. as in [83G122]. | 82Z254 |
| | $O_2^- + 1,2\text{-}C_6H_4(OH)_2 \rightarrow$ | 0.5–9 | $(2.7 \pm 0.3) \times 10^5$ | s.f., opt. | D.k. at 245 nm; soln. prepd. as in [83G122]. | 82Z254 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 190 | **Ceruloplasmin** | | | | | |
| | $HO_2/O_2^-$ + Ceruloplasmin → | 7.8 | $1.8 \times 10^6$ | p.r., opt. | D.k. at 610 nm in air-satd. soln. contg. formate (type 1 $Cu^{II}$). No change in absorption at 330 nm and no marked increase in $O_2^-$ decay at 250 nm. Authors note that this rate may be due to $CO_2^-$ radicals and not $O_2^-$. | 80A220 |
| 191 | **Citrate ion** | | | | | |
| | $O_2^-$ + $R(CO_2^-)_3$ → | 10.1 | <0.14 | $e$-r., s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and $10^{-4}$ mol L$^{-1}$ EDTA and 0.01–0.1 mol L$^{-1}$ citrate; no reaction | 770046 |
| 192 | **Crocin** | | | | | |
| | $O_2^-$ + crocin → | 5.9 | | X-r. | No bleaching in oxygenated soln. contg. Na formate; at low pH bleaching occurs indicating $HO_2$ reactivity. | 82R027 |
| 193 | **4-Cyanophenyl-*N*-*tert*-butylnitrone** | | | | | |
| | $HO_2/O_2^-$ + 4-CN-PBN → $OH^-$ + 4-CN-PBN(OOH) | | <$6 \times 10^6$ | p.r., opt. | C.k. in $O_2$-satd. soln. contg. *tert*-BuOH or formate; obs. $Q^{\cdot-}$ at 420 nm; rel. to $k(O_2^- + Q) = 1.0 \times 10^9$; Cf. [80A176], this value seems high. | 82A184 |
| 194 | **Cyclohexylperoxy** | | | | | |
| | $HO_2$ + $c$-$C_6H_{11}O_2\cdot$ → $c$-$C_6H_{11}O_2H$ + $O_2$ | 1.85 | $2.26 \times 10^6$ | γ-r., chem. | Detd. $H_2O_2$ and $RO_2H$ yields; assume $k(RO_2 + RO_2) = 2.7 \times 10^6$; pH not given. | 670737 |
| | $O_2^-$ + $c$-$C_6H_{11}O_2\cdot$ → $c$-$C_6H_{11}O_2H$ + $O_2$ | 6–8 | $2.54 \times 10^8$ | γ-r., chem. | Detd. from pH dependence of $H_2O_2$ and $RO_2H$ yields; assume $k(RO_2 + RO_2) = 2.7 \times 10^6$. | 670737 |
| 195 | **Cysteine, p$K_a$ = —2, 8.14, 10.34** | | | | | |
| | $HO_2$ + $CysH^+$ → | 1.4 | <601.0 ± 85.0 | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ cysteine; also detd. by $O_2$-consumption. upper limit. | 79A358 |
| | $HO_2/O_2^-$ + Cys → | 3–5.1 | ~$1.8 \times 10^4$ | γ-r., chem. | Obs. increase in $G(H_2O_2)$ with pH. | 740188 |
| | | 7 | >$5 \times 10^4$ | γ-r., chem. | Obs. $G(H_2O_2)$ as function of dose. | 700882 |
| | $O_2^-$ + Cys → | 10.9 | <15 ± 2.0 | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.05 mol L$^{-1}$ cysteine; no reaction. | 79A358 |
| 196 | **L-Cystine, p$K_a$ = 7.85, 9.85, 11.8, 12.4** | | | | | |
| | $O_2^-$ + Cyt → | 10.0 | <0.40 ± 0.07 | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and $5 \times 10^{-4}$ mol L$^{-1}$ cystine; no reaction. | 79A358 |
| 197 | **Cytochrome C (ferri), p$K_a$ = 7.45, 9.2** | | | | | |
| | $HO_2$ + Cyt C ($Fe^{3+}$) → $O_2$ + Cyt C ($Fe^{2+}$) | 1.2–6.2 | | p.r., opt. | No reaction obs. | 753093 |
| | | 1.84 | | p.r., opt. | No reaction obs. (550 nm); c.k. | 710327 |
| | $O_2^-$ + Cyt C ($Fe^{3+}$) → $O_2$ + Cyt C ($Fe^{2+}$) | | ~$6 \times 10^4$ | phot., s.f., opt. | D.k. at 550 nm in soln. contg. 10.2 mol L$^{-1}$ EtOH. pH not certain in EtOH/$H_2O$ mixture. | 82A021 |
| | | 7.8 | $6 \times 10^5$ | p.r., opt. | D.k. at 250 nm. | 82A446 |
| | | 7.3 | $5.84 \times 10^5$ | f.p., opt. | D.k. in soln. contg. $2 \times 10^{-2}$ mol L$^{-1}$ tetramethylenediamine, $10^{-5}$ mol L$^{-1}$ EDTA, $6 \times 10^{-5}$ mol L$^{-1}$ FMN and $1–4 \times 10^{-5}$ mol L$^{-1}$ cyt C. | 82A269 |
| | | 7.8 | $(2.6 \pm 0.1) \times 10^5$ | p.r., opt. | P.b.k. at 550 nm in soln. contg. $5 \times 10^{-2}$ mol L$^{-1}$ phosphate, $1 \times 10^{-4}$ mol L$^{-1}$ EDTA; pH dependence and effect of added $Cu^{2+}$, see FIGURE 2. | 82A281 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| | | 7.2 | $8.0 \times 10^5$ | p.r., opt. | D.k. at 550 nm in soln. contg. *tert*-BuOH or glycerol as OH scavenger; $k$ decreases with added detergent; $k = 5 \times 10^4$ extrapolated to infinite SDS concn. | 82N062 |
| | | ~7 | $8.0 \times 10^5$ | p.r., opt. | D.k. at 550 nm in soln. contg. 0.1 mol L$^{-1}$ formate and $2 \times 10^{-3}$ mol L$^{-1}$ phosphate; observed rate. | 79A312 |
| | | 9.0 | $(2.6 \pm 0.2) \times 10^5$ | p.r., opt. | P.b.k. at 550 nm in air-satd. soln. contg. 0.01 mol L$^{-1}$ formate and $10^{-4}$ mol L$^{-1}$ EDTA. | 78A361 |
| | | 9.0 | $(2.6 \pm 0.2) \times 10^5$ | $e$-r., s.f., opt. | P.b.k. at 550 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and $2 \times 10^{-4}$ mol L$^{-1}$ EDTA and 5–20 $\times 10^{-5}$ mol L$^{-1}$ cyt C; cor. for $O_2^-$ decay. | 770046 |
| | | 7.4<br>8.5 | $(5 \pm 0.3) \times 10^5$<br>$(2 \pm 0.2) \times 10^5$ | p.r., opt. | D.k. at 550 nm in $O_2$–satd. soln. contg. 0.1 mol L$^{-1}$ Na formate; also in $D_2O$ (no isotope effect). | 771096 |
| | | 6.6<br>7.3<br>8.7<br>9.2 | $6.2 \times 10^5$<br>$5.0 \times 10^5$<br>$2.6 \times 10^5$<br>$2.0 \times 10^5$ | p.r., opt. | D.k. at 450 and 550 nm in soln. contg. Na formate and $O_2$; $I = 0.1$; $E_a$, $\Delta S^\ddagger$, $\Delta H^\ddagger$ and $I$ discussed. | 761127 |
| | | 7.1 | $(3.1 \pm 0.1) \times 10^6$ (cor. for $I$) | p.r., opt. | P.b.k. at 550 nm in soln. contg. $10^{-3}$ mol L$^{-1}$ phosphate buffer, $2 \times 10^{-3}$ mol L$^{-1}$ formate and $2 \times 10^{-5}$ mol L$^{-1}$ EDTA and $2 \times 10^{-3}$ mol L$^{-1}$ $O_2$; $I = 0.1$; observed rate. | 761163 |
| | | 7<br>9.3 | $2.4 \times 10^6$<br>$1.5 \times 10^5$ | p.r., opt. | P.b.k. $k_{obs}$ vs pH given for pH 6.0–10.5. | 751012 |
| | | 4.7–6.7 | $(1.4 \pm 0.15) \times 10^6$ | p.r., opt. | P.b.k. at 550 nm; from pH effect $k = 3.0 \times 10^4$ for the form present above pH 7.45 ($pK_a$ cyt C = 7.45, 9.2). The form present above pH 9.2 does not react. | 753093 |
| | | 8.5 | $1.1 \times 10^5$ | p.r., opt. | P.b.k. at 550 nm; at pH 10.4 $k = 8 \times 10^3$. | 710327 |
| | | 8.4 | $1.6 \times 10^5$ | esr | D.k.; $O_2^-$ from tetraacetylriboflavin + $O_2$. Observed rate. | 699128 |
| 198 | **Cytochrome C, acetylated**<br>$HO_2/O_2^-$ + Ac-cyt C → | ~7 | $3.5 \times 10^5$ | p.r., opt. | D.k. at 550 nm in soln. contg. 0.1 mol L$^{-1}$ formate; $I = 0.1$. | 79A312 |
| 199 | **Cytochrome C, carboxymethylated**<br>$O_2^-$ + Cxm-cyt C → | | | p.r. | No reaction obs. | 79A312 |
| 200 | **Cytochrome C, succinylated**<br>$O_2^-$ + Succ-cyt C → | | | p.r. | No reaction obs. | 79A312 |
| 201 | **Cytochrome C (ferro)**<br>$HO_2/O_2^-$ + Cyt C ($Fe^{2+}$) → $H_2O_2$ + Cyt C ($Fe^{3+}$) | 5.3 | $5 \times 10^5$ to $5 \times 10^6$ | p.r., opt. | D.k. at 550 nm; estimated value studied at a single pH. | 753093 |
| 202 | **Cytochrome P-450**<br>$O_2^-$ + cyt P-450 → | | | p.r. | No reaction obs. | 79A036 |
| 203 | **Cytochrome f ($Fe^{3+}$)**<br>$O_2^-$ + Cyt f ($Fe^{3+}$) → Cyt f ($Fe^{2+}$) | 7.8 | $6.1 \times 10^6$ | enz., opt. | Xanthine-xanthine oxidase system; soln. cont. phosphate ($5 \times 10^{-2}$ mol L$^{-1}$) and EDTA ($10^{-4}$ mol L$^{-1}$). | 77R240 |
| 204 | **Dialuric acid**<br>$HO_2/O_2^-$ + $AlH_2$ → $H_2O_2$ + ·AlH | 5.7 | $\leqslant 10^3$ | p.r., opt. | Buildup and decay of dialuric acid (275 nm) and semiquinone at 310 and 370 nm in soln contg. 0.1 mol L$^{-1}$ formate ion, $1.46 \times 10^{-4}$ mol L$^{-1}$ $O_2$, $5 \times 10^{-3}$ mol L$^{-1}$ alloxan; assumed mechanism, $\epsilon$(·AlH) = 4000(275), 4900(310) and 1900(370 nm), $\epsilon$(Al) — 16000(275) and 160(310 nm). | 81A271 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 205 | **Diamide** *(Diazenedicarboxylic acid bisdimethylamide)* | | | | | |
| | $HO_2/O_2^- + ((CH_3)_2NCON=)_2 \rightarrow$ | ~7 | $<10^6$ | p.r., opt. | P.b.k. at 400 nm in soln. contg. 0.1 mol L$^{-1}$ formate and $10^{-4}$ mol L$^{-1}$ substrate; <3% electron transfer. | 751194 |
| 206 | **1,4-Diazabicyclo[2.2.2]octane** | | | | | |
| | $O_2^- +$ DABCO $\rightarrow$ | 7.2 | | p.r. | D.k. at 270 nm; no reaction obs. | 78R103 |
| 207 | **2,5-Dichloro-*p*-benzoquinone** | | | | | |
| | $O_2^- + 2,5\text{-}Cl_2Q \rightarrow$ | 7.0 | $1.1 \times 10^9$ | p.r., opt. | P.b.k. at 430 nm in soln. contg. $5 \times 10^{-5}$ mol L$^{-1}$ quinone. | 730068 |
| 208 | **2,5-Dichlorohydroquinone** | | | | | |
| | $O_2^- + Cl_2C_6H_2(OH)_2 \rightarrow$ $2,5\text{-}Cl_2Q^{\cdot -} + H_2O_2$ | 7.0 | $1.3 \times 10^7$ | p.r., opt. | P.b.k. in $O_2$-satd. soln. contg. $10^{-3}$ mol L$^{-1}$ quinone, 0.1 mol L$^{-1}$ formate. | 751011 |
| 209 | **2,6-Dichloroindophenolate ion** | | | | | |
| | $O_2^- +$ DCIP$^- \rightarrow$ $O_2 +$ DCIP$^{\cdot 2-}$ | 7.0 | $(2.14 \pm 0.05) \times 10^8$ | p.r., opt. | C.k., rel. to $k(O_2^- + \text{SOD}) = 3.7 \times 10^9$. | 79A240 |
| | | ~7 | $\sim 1.5 \times 10^8$ | p.r., opt. | D.k. at 600 nm (oxidized DCIP) in $O_2$-satd. soln. contg. *tert*-BuOH and $(1\text{-}6) \times 10^{-4}$ mol L$^{-1}$ DCIP. | 761056 |
| | | ~7 | $(1.7 \pm 0.3) \times 10^8$ | p.r., opt. | D.k. at 430 nm in soln. contg. $5 \times 10^{-5}$ mol L$^{-1}$ substrate; rel. to $k(O_2^- + Q) = 9 \times 10^8$. | 761056 |
| 210 | **3,4-Dihydroxyacetophenone** | | | | | |
| | $O_2^- + (HO)_2C_6H_3COCH_3 \rightarrow$ | 7 | $(2.94 \pm 0.22) \times 10^7$ | p.r. | C.k.; rel. to $k(O_2^- + \text{DCIP}^-) = 2.14 \times 10^8$. | 79A303 |
| 211 | **3,4-Dihydroxybenzaldehyde** | | | | | |
| | $O_2^- + (HO)_2C_6H_3CHO \rightarrow$ | 7 | $(1.40 \pm 0.03) \times 10^7$ | p.r. | C.k.; rel. to $k(O_2^- + \text{DCIP}^-) = 2.14 \times 10^8$. | 79A303 |
| 212 | **4,5-Dihydroxy-*m*-benzenedisulfonate ion** | | | | | |
| | $HO_2/O_2^- + (HO)_2C_6H_2(SO_3)_2^{2-} \rightarrow$ | | $1.0 \times 10^7$ | p.r. | Neutral pH assumed; no buffer; rel. to $k(O_2^- + \text{DCIP}^-) = 2.1 \times 10^8$. | 79A014 |
| | $O_2^- + (HO)_2C_6H_2(SO_3)_2^{2-} \rightarrow$ | 7 | $1.5 \times 10^8$ | p.r, opt. | C.k.; rel. to $k(O_2^- + Q) = 9 \times 10^8$. | 751087 |
| | | 7 | $5 \times 10^8$ | p.r., opt. | P.b.k. at 400 nm. | 751087 |
| 213 | **2,5-Dihydroxybenzoic acid** | | | | | |
| | $HO_2 + (HO)_2C_6H_3CO_2H \rightarrow$ | 0.5–1.5 | $(3.9 \pm 0.3) \times 10^4$ | s.f., opt. | D.k. at 245–255 nm; soln. prepd. as in [83G122]. | 82Z254 |
| 214 | **5,8-Dihydroxy-1,4-naphthoquinone** | | | | | |
| | $HO_2/O_2^- + NQ(OH)_2 \rightarrow O_2 +$ $\cdot NQ(OH)_2^-$ | 5.2 | $(5.8 \pm 0.5) \times 10^8$ | p.r., opt. | P.b.k. at 380 nm in air-satd. soln. contg. 0.1 mol L$^{-1}$ formate and phosphate buffer; from equilibrium constant = 5.6, $k_{\text{reverse}} = (1.1 \pm 0.2) \times 10^8$. | 83A039 |
| 215 | **2,3-Dimethyl-1,4-benzoquinone** | | | | | |
| | $O_2^- + 2,3\text{-}(CH_3)_2Q \rightarrow$ $2,3\text{-}(CH_3)_2Q^{\cdot -} + O_2$ | 7 | $(4.5 \pm 1) \times 10^8$ | p.r., opt. | P.b.k. | 730125 |
| 216 | **2,5-Dimethyl-1,4-benzoquinone** | | | | | |
| | $O_2^- + 2,5\text{-}(CH_3)_2Q \rightarrow$ $[2,5\text{-}(CH_3)_2Q]^{\cdot -} + O_2$ | 7.2 | $1.7 \times 10^8$ | p.r., opt. | P.b.k. (semiquinone) in soln. contg. 0.1 mol L$^{-1}$ Na formate and 1.25–12.5 $\times 10^{-4}$ mol L$^{-1}$ $O_2$. | 761063 |
| | | 7.0 | $7.5 \times 10^8$ | p.r., opt. | P.b.k. at 430 nm in soln. contg. $5 \times 10^{-5}$ mol L$^{-1}$ quinone. | 730068 |
| | | 7 | $(3.6 \pm 1) \times 10^8$ | p.r., opt. | P.b.k. | 730125 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 217 | **2,6-Dimethylbenzoquinone** | | | | | |
| | $O_2^- + 2,6\text{-}(CH_3)_2Q \rightarrow [2,6\text{-}(CH_3)_2Q]^{\cdot -} + O_2$ | 7 | $(5.8 \pm 1) \times 10^8$ | p.r., opt. | P.b.k. | 730125 |
| 218 | **1,1'-Dimethyl-4,4'-bipyridinium radical ion (1+)** | | | | | |
| | $HO_2 + MV^{\cdot +} \rightarrow$ | 3.5 | $2.1 \times 10^9$ | p.r., opt. | D.k. in soln. contg. 4–16 $\times 10^{-2}$ mol L$^{-1}$ $H_2O_2$; $G(HO_2) = 5.98$, 6.51 assumed from $OH + H_2O_2 \rightarrow HO_2$. | 83A043 |
| | $O_2^- + MV^{\cdot +} \rightarrow$ | 7 | $2.8 \times 10^9$ | p.r., opt. | D.k. in soln. contg. 4–16 $\times 10^{-2}$ mol L$^{-1}$ $H_2O_2$; $G(HO_2) = 6.15$ assumed from $OH + H_2O_2 \rightarrow HO_2$. | 83A043 |
| | | 6.8 | $(9.2 \pm 1.1) \times 10^8$ | p.r. | Ar-satd. soln. contg. $10^{-3}$ mol L$^{-1}$ $MV^{2+}$ $2Cl^-$ and 0.1 mol L$^{-1}$ Na formate and ~0.3% $O_2$. | 78A321 |
| | | | $6.5 \times 10^8$ | p.r., opt. | Calcd. from d.k.; $k(O_2 + MV^{\cdot +}) = 7.7 \times 10^8$. | 731074 |
| 219 | **2,3-Dimethylnaphthoquinone** | | | | | |
| | $O_2^- + 2,3\text{-}(CH_3)_2NQ \rightarrow 2,3\text{-}(CH_3)_2NQ^{\cdot -} + O_2$ | 7 | $4 \times 10^6$ | p.r., opt. | Detd. from equil. const. and d.k. of semiquinone in soln. contg. $10^{-3}$ mol L$^{-1}$ quinone, 5 mol L$^{-1}$ 2-PrOH and 1 mol L$^{-1}$ acetone. | 730125 |
| 220 | **5,5-Dimethyl-1-pyrroline-*N*-oxide** | | | | | |
| | $HO_2/O_2^- + DMPO \rightarrow$ | | $6.6 \times 10^3$ | esr | Calcd. from effect of pH (5–9) on $k_{obs}$; c.k. with SOD; rel. to $k(O_2^- + Fe^{3+}$ cyt C) = $6 \times 10^5$. | 80A176 |
| | $O_2^- + DMPO \rightarrow$ | 7.8 | 10 | enz., esr | Spin trapping; rel. to $k(O_2^- + TMPO) = 7$. | 80A176 |
| | | 8.0 | 15.7 | phot., esr | Spin trapping; c.k. with SOD; rel. to $k(O_2^- + Fe^{3+}$ cyt C) = $6 \times 10^5$. Studied from pH 5–9. | 80A176 |
| 221 | **Diphenoquinone** | | | | | |
| | $O_2^- + O{=}C_6H_4C_6H_4{=}O \rightarrow {\cdot}OC_6H_4C_6H_4O^- + O_2$ | 7.0 | $1.4 \times 10^9$ (±10%) | p.r., opt. | P.b.k. at 400 nm in soln. contg. $5 \times 10^{-5}$ mol L$^{-1}$ quinone. | 730068 |
| 222 | **1,1'-Diphenyl-4,4'-bipyridinium radical ion (1+)** | | | | | |
| | $O_2^- + BP^{\cdot +} \rightarrow$ | | $(6.2 \pm 2.0) \times 10^9$ | p.r. | Ar-satd. soln. contg. $10^{-3}$ mol L$^{-1}$ $BP^{2+}$ $2Cl^-$ and 0.1 mol L$^{-1}$ formate and ~0.3% $O_2$; pH not given. | 78A321 |
| 223 | **Dithiothreitol** | | | | | |
| | $HO_2/O_2^- + DTT \rightarrow$ | 7.8 | $1.0 \times 10^6$ | enz., opt. | Xanthine-xanthine oxidase system; c.k., rel. to $k(HO_2/O_2^- +$ adrenaline) = $4 \times 10^4$. | 76R183 |
| 224 | **Duroquinone** | | | | | |
| | $O_2^- + DQ \rightarrow DQ^{\cdot -} + O_2$ | 7 | $1.0 \times 10^7$ | p.r., opt. | D.k. (semiquinone) in soln. contg. Na formate and $O_2$. | 751090 |
| | | 7 | $(4.5 \pm 1.5) \times 10^6$ | p.r., opt. | Detd. from equil. const. and d.k. of semiquinone in soln. contg. 5 mol L$^{-1}$ 2-PrOH and 2 mol L$^{-1}$ acetone. | 730125 |
| 225 | **Ethylene** | | | | | |
| | $HO_2/O_2^- + H_2C{=}CH_2 \rightarrow$ | | $2 \times 10^5$ | γ-r., chem. | C.k.; pH not given; rel. to $k(HO_2 + Fe^{2+})$ calcd. from value taken from [730038]. | 670037 |
| 226 | **1,1'-Ethylene-2,2'-bipyridinium radical ion (1+)** | | | | | |
| | $O_2^- + BP^{\cdot +} \rightarrow$ | | $(4.8 \pm 0.5) \times 10^8$ | p.r. | Ar-contg. soln. contg. $10^{-3}$ mol L$^{-1}$ $BP^{2+}$ $2Cl^-$ and 0.1 mol L$^{-1}$ Na formate and ~0.3% $O_2$; pH not given. | 78A321 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 227 | **Ethylenediaminetetraacetate ion** | | | | | |
| | $O_2^- + [CH_2N(CH_2CO_2^-)_2]_2 \rightarrow$ | 9.9 | <0.01 | *e*-r., s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and 0.01–0.1 mol L$^{-1}$ EDTA; no reaction obs. | 770046 |
| 228 | **2-Ethyl-1-hydroxy-2,5,5-trimethyl-3-oxazolidine** | | | | | |
| | $HO_2/O_2^- +$ OXANO $\rightarrow$ | 7.8 | $6.7 \times 10^3$ | enz, opt. | C.k. in xanthine oxidase system, rel. to $k(O_2^- +$ cyt C$) = 6 \times 10^5$. | 82R165 |
| 229 | **Ferredoxin (spinach)** | | | | | |
| | $HO_2/O_2^-$ + Ferredoxin $\rightarrow$ | 7.7 | $<10^4$ | p.r., opt. | D.k. in soln. contg. $6.5 \times 10^{-2}$ mol L$^{-1}$ phosphate buffer. | 78R208 |
| 230 | **Flavin adenine dinucleotide semiquinone** | | | | | |
| | $O_2^-$ + FADH· $\rightarrow$ | 7 | $(2.2 \pm 0.2) \times 10^8$ | p.r., opt. | D.k. at 540 nm in aerated soln. contg. 0.01 mol L$^{-1}$ formate ion and $8 \times 10^{-5}$ mol L$^{-1}$ flavin. | 81A375 |
| 231 | **Flavin mononucleotide semiquinone** | | | | | |
| | $HO_2$ + FMNH· $\rightarrow$ | 2.5–4.0 | $6.2 \times 10^8$ | p.r., opt. | D.k. at 540 nm in aerated soln. contg. 0.01 mol L$^{-1}$ formate and $8 \times 10^{-5}$ mol L$^{-1}$ flavin. Studied from pH 2–8. | 81A375 |
| | $O_2^-$ + FMNH· $\rightarrow$ | 7 | $(3.2 \pm 0.2) \times 10^8$ | p.r., opt. | D.k. at 540 nm in aerated soln. contg. 0.01 mol L$^{-1}$ formate ion and $8 \times 10^{-5}$ mol L$^{-1}$ flavin. Studied as a function of pH 2–8. | 81A375 |
| 232 | **Formate ion** | | | | | |
| | $O_2^- + HCO_2^- \rightarrow$ | 10.1 | <0.01 | *e*-r., s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. $5 \times 10^{-4}$ mol L$^{-1}$ formate and $1 \times 10^{-4}$ mol L$^{-1}$ EDTA; no reaction obs. | 770046 |
| 233 | **Fumarate ion** | | | | | |
| | $O_2^-$ + *trans*-$^-O_2CCH = CHCO_2^- \rightarrow$ | 10.1 | <0.10 | *e*-r., s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.01–0.1 mol L$^{-1}$ fumarate, 0.2 mol L$^{-1}$ formate and $10^{-4}$ mol L$^{-1}$ EDTA; no reaction obs. | 770046 |
| 234 | **L-Glutamic acid, p$K_a$ = 2.06, 4.26, 9.85** | | | | | |
| | $HO_2$ + Glu $\rightarrow$ | 1.6 | $<30.0 \pm 6.0$ | $\gamma$-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ glutamic acid; upper limit. | 79A358 |
| | $O_2^-$ + Glu $\rightarrow$ | 8.7 | $<0.39 \pm 0.07$ | $\gamma$-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.025 mol L$^{-1}$ glutamic acid; no reaction obs. | 79A358 |
| 235 | **L-Glutamine, p$K_a$ = 2.17, 9.13** | | | | | |
| | $HO_2$ + Gln $\rightarrow$ | 1.5 | $<23.0 \pm 6.0$ | $\gamma$-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ glutamine, upper limit. | 79A358 |
| | $O_2^-$ + Gln $\rightarrow$ | 10.0 | $<0.25 \pm 0.05$ | $\gamma$-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ glutamine no reaction obs. | 79A358 |
| 236 | **Glutathione, p$K_a$ = 2, 3.59, 8.75, 9.65** | | | | | |
| | $HO_2/O_2^-$ + GSH $\rightarrow$ | 7.8 | $6.7 \times 10^5$ | enz., opt. | Xanthine-xanthine oxidase system; c.k., rel. to $k(HO_2/O_2^- +$ adrenaline$) = 4 \times 10^4$. | 76R183 |
| 237 | **Glyceraldehyde-3-phosphate dehydrogenase-NADH complex** | | | | | |
| | $HO_2$ + GPDH-NADH $\rightarrow$ | 4.8–9.5 | $2.00 \times 10^7$ | p.r., opt. | D.k. in soln. contg. 0.05 mol L$^{-1}$ phosphate, $10^{-5}$ mol L$^{-1}$ EDTA, $10^{-4}$ mol L$^{-1}$ NADH and $2.5 \times 10^{-4}$ mol L$^{-1}$ $O_2$ and $6.48 \times 10^{-5}$ mol L$^{-1}$ enzyme; estd. from $k_{obs}$ vs pH; $O_2^-$ unreactive. | 80A413 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 238 | **Glycine, p$K_a$ = 2.35, 9.78** | | | | | |
| | $HO_2$ + Gly → | 1.5 | $<48.6 \pm 4.0$ | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ glycine; upper limit. | 79A358 |
| | $O_2^-$ + Gly → | 8.8 | $<0.42 \pm 0.12$ | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ glycine no reaction obs. | 79A358 |
| 239 | **Hemocyanin** | | | | | |
| | $HO_2/O_2^-$ + Hemocyanin → | 8.0 | $<10^6$ | p.r., opt. | No reaction obs. at 290 nm in $O_2$-satd. soln. contg. $2 \times 10^{-2}$ mol L$^{-1}$ Na formate. | 761021 |
| 240 | **L-Histidine, p$K_a$ = 1.80, 6.04, 9.33** | | | | | |
| | $HO_2$ + His → | 1.8 | $<95.0 \pm 14.0$ | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.05 mol L$^{-1}$ histidine; upper limit. | 79A358 |
| | $O_2^-$ + His → | 10.0 | $<1.00 \pm 0.21$ | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.15 mol L$^{-1}$ histidine no reaction obs. | 79A358 |
| 241 | **Homocysteine** | | | | | |
| | $HO_2/O_2^-$ + Hcy → | 7.8 | $4.6 \times 10^5$ | enz., opt. | Xanthine-xanthine oxidase system; c.k., rel. to $k(HO_2/O_2^-$ + adrenaline) = $4 \times 10^4$. | 76R183 |
| 242 | **1-Hydroperoxy-2-cyclooctene** | | | | | |
| | $HO_2$ + $c$-$C_8H_{13}O_2H$ → | | | s.f., opt. | D.k. at 250–270 nm in 80% EtOH soln. with $5 \times 10^{-2}$ mol L$^{-1}$ $H_2SO_4$, $1 \times 10^{-5}$ mol L$^{-1}$ EDTA, $1.2 \times 10^{-3}$ mol L$^{-1}$ $O_2$. Peroxide concn. $4.0 \times 10^{-2}$ mol L$^{-1}$. No reaction obs. | 84A909 |
| | $O_2^-$ + $c$-$C_8H_{13}O_2H$ → | | | s.f., opt. | D.k. at 250–270 nm in 80% EtOH soln. with $10^{-2}$ mol L$^{-1}$ KOH,, $1 \times 10^{-5}$ mol L$^{-1}$ EDTA, $1.2 \times 10^{-3}$ mol L$^{-1}$ $O_2$. Peroxide concn. $3 \times 10^{-3}$ mol L$^{-1}$. No reaction obs. | 84A909 |
| 243 | **Hydroquinone** | | | | | |
| | $HO_2$ + 1,4-$C_6H_4(OH)_2$ → ·$OC_6H_4OH$ + $H_2O_2$ | 0.4–3.5 | $(0.85 \pm 0.1) \times 10^4$ | f.p., opt. | P.b.k. at 290 nm; value could be twice as fast, see paper for discussion. | 79A340 |
| | $HO_2/O_2^-$ + 1,4-$C_6H_4(OH)_2$ → $Q^{\cdot -}$ + $H_2O_2$ | ~7 | $1.7 \times 10^7$ | p.r. | Soln. cont. $10^{-3}$ mol L$^{-1}$ $QH_2$. | 751011 |
| | | 7.0 | $(1.6 \pm 0.1) \times 10^7$ | p.r., opt. | P.b.k. at 430 nm in soln. contg. $10^{-3}$ mol L$^{-1}$ $QH_2$, $1.3 \times 10^{-3}$ mol L$^{-1}$ $O_2$ and 1 mol L$^{-1}$ *tert*-BuOH.. | 730068 |
| 244 | **1-Hydroxyethyldioxy** | | | | | |
| | $HO_2/O_2^-$ + $CH_3C(O_2)HOH$ → $CH_3CO_2H$ + $H_2O$ + $O_2$ | 3 | $\sim 10^7$ | | Calcd. from product distribution and other reaction rates. | 83A056 |
| 245 | **6-Hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid** | | | | | |
| | $HO_2$ + HTC-$CO_2H$ → | acid | $(2.02 \pm 0.18) \times 10^5$ | s.f., opt. | D.k. at 254 nm; carried out in 85% EtOH contg. 0.022 mol L$^{-1}$ $H_2SO_4$. | 82Z254 |
| 246 | **6-Hydroxy-2,5,7,8-tetramethylchroman-2-carboxylate ion** | | | | | |
| | $HO_2/O_2^-$ + HTC-$CO_2^-$ → | 7.4 | $1.7 \times 10^4$ | enz., opt. | D.k. at 249.6 nm in xanthine-xanthine oxidase system contg. $10^{-4}$ mol L$^{-1}$ EDTA, $10^{-1}$ mol L$^{-1}$ phosphate buffer and $2 \times 10^{-4}$ mol L$^{-1}$ substrate. | 75R176 |
| | $O_2^-$ + HTC-$CO_2^-$ → | alk. | | s.f., opt. | D.k. at 254 nm; carried out in 85% EtOH contg. 0.01 mol L$^{-1}$ KOH. No reaction obs. | 82Z254 |
| 247 | **3-(6-Hydroxy-2,5,7,8-tetramethylchroman-2-yl)propionate ion** | | | | | |
| | $HO_2/O_2^-$ + HTC-$CH_2CH_2CO_2^-$ → | 7.4 | $5.9 \times 10^3$ | enz., opt. | D.k. at 248.9 nm, in soln. contg. $4 \times 10^{-4}$ mol L$^{-1}$ substrate, $1 \times 10^{-4}$ mol L$^{-1}$ EDTA, $4 \times 10^{-5}$ mol L$^{-1}$ xanthine, and 0.1 mol L$^{-1}$ phosphate buffer. | 78R210 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 248 | **Imidazole, p$K_a$ = 6.96** | | | | | |
| | $O_2^- + Im \rightarrow$ | 10.1 | <0.02 | *e*-r., s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and $10^{-4}$ mol L$^{-1}$ EDTA and 0.01–0.1 mol L$^{-1}$ mol L$^{-1}$ imidazole; no reaction obs. | 770046 |
| 249 | **Indigodisulfonate ion** | | | | | |
| | $HO_2 + IDS^{2-} \rightarrow O_2 + IDS^{\cdot 3-} + H^+$ | 0.4 | $2.0 \times 10^4$ | γ-r., opt. | C.k.; $G(HO_2) = 3.6$; value recalcd. using $k(HO_2 + HO_2) = 8.6 \times 10^5$. | 680059 |
| | $O_2^- + IDS^{2-} \rightarrow O_2 + IDS^{\cdot 3-}$ | 7 | $9 \times 10^5$ | p.r., opt. | D.k. of $IDS^{2-}$ in soln. contg. Na formate and oxygen | 751090 |
| 250 | **Indigotetrasulfonate ion** | | | | | |
| | $HO_2 + ITS^{4-} \rightarrow O_2 + ITS^{\cdot 5-}$ | 0.4 | $1.8 \times 10^3$ | γ-r., opt. | C.k.; $G(HO_2) = 3.6$; value recalcd. using $k(HO_2 + HO_2) = 8.6 \times 10^5$. | 680059 |
| 251 | **Indigotrisulfonate ion** | | | | | |
| | $HO_2 + ITS^{3-} \rightarrow O_2 + ITS^{\cdot 4-}$ | 0.4 | $1.1 \times 10^4$ | γ-r., opt. | C.k.; $G(HO_2) = 3.6$; value recalcd. using $k(HO_2 + HO_2) = 8.6 \times 10^5$. | 680059 |
| 252 | **Indomethacin** | | | | | |
| | $HO_2/O_2^- + In \rightarrow$ | 7.0 | $(2.6 \pm 0.1) \times 10^6$ | p.r., opt. | D.k. at 250 nm in soln. contg. $10^{-2}$ mol L$^{-1}$ formate. | 80A201 |
| 253 | **DL-Isoleucine, p$K_a$ = 2.318, 9.758** | | | | | |
| | $HO_2 + Ile \rightarrow$ | 1.4 | $<38.9 \pm 5.0$ | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and 5 $\times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ isoleucine; upper limit. | 79A358 |
| | $O_2^- + Ile \rightarrow$ | 8.0 | $<2.00 \pm 0.40$ | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and 5 $\times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ mol L$^{-1}$ isoleucine; no reaction. | 79A358 |
| 254 | **Laccase** | | | | | |
| | $HO_2/O_2^- +$ Laccase $\rightarrow$ | 6.0 | $\geq 2 \times 10^6$ | p.r., opt. | Transient adduct obs. in soln. contg. 0.01 mol L$^{-1}$ potassium phosphate, $95 \times 10^{-6}$ mol L$^{-1}$ laccase, and 0.1 mol L$^{-1}$ formate; addn. followed by $Cu^{2+}$ redn.; complex kinetics. | 82A422 |
| 255 | **Lactate ion** | | | | | |
| | $O_2^- + CH_3CHOHCO_2^- \rightarrow$ | 10.0 | <0.50 | *e*-r., s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and $10^{-4}$ mol L$^{-1}$ EDTA and 0.01–0.1 mol L$^{-1}$ lactate; no reaction. | 770046 |
| 256 | **L-Leucine, p$K_a$ = 2.328, 9.744** | | | | | |
| | $HO_2 + Leu \rightarrow$ | 1.4 | $<23.0 \pm 4.0$ | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and 5 $\times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ leucine; upper limit. | 79A358 |
| | $O_2^- + Leu \rightarrow$ | 9.9 | $<0.21 \pm 0.02$ | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and 5 $\times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ leucine; no reaction. | 79A358 |
| 257 | **Linoleate hydroperoxide** | | | | | |
| | $HO_2/O_2^- + HO_2L^- \rightarrow$ | | $7.4 \times 10^3$ | enz, opt. | Rate inferred from ratio of SOD inhibition of linoleate oxidation, $HO_2$ may be reactive form. | 82R039 |
| | | 8.1 | $7 \times 10^3$ | enz, opt. | P.b.k. at 235 nm in soln. contg. $6.3 \times 10^{-8}$ mol L$^{-1}$ xanthine oxidase, $4.8 \times 10^{-2}$ mol L$^{-1}$ acetaldehyde, $10^{-3}$ mol L$^{-1}$ linoleic acid and phosphate. | 78R207 |
| | $O_2^- + HO_2L^- \rightarrow$ | 7 | | p.r. | No reaction obs. in soln. contg. formate and $O_2$. | 79A295 |
| 258 | **Linoleate ion** | | | | | |
| | $O_2^- + L^- \rightarrow$ | | $10^{-2}$–$10^{-1}$ | s.f., opt. | 85% v/v ethanolic soln.; d.k. at 240–270 nm. Strongly alk. conditions (0.001–0.01 mol L$^{-1}$ KOH). Negligible reaction. | 83A087 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 259 | **Linoleic acid** | | | | | |
| | $HO_2 + LH \rightarrow$ | | $(1.18 \pm 0.20) \times 10^3$ | s.f., opt. | 85% v/v ethanolic soln.; d.k. at 240–270 nm; 0.05 mol L$^{-1}$ $H_2SO_4$. | 83A087 |
| 260 | **Linoleic acid hydroperoxide** | | | | | |
| | $HO_2 + HO_2LH \rightarrow$ | | | s.f., opt. | D.k. at 250–270 nm in 80% EtOH soln. with $5 \times 10^{-2}$ mol L$^{-1}$ $H_2SO_4$, $1 \times 10^{-5}$ mol L$^{-1}$ EDTA, $1.2 \times 10^{-3}$ mol L$^{-1}$ $O_2$. Peroxide concn. $2 \times 10^{-3}$ mol L$^{-1}$. No reaction obs. | 84A909 |
| | $O_2^- + HO_2LH \rightarrow$ | | | s.f., opt. | D.k. at 250–270 nm in 80% EtOH soln. with $10^{-2}$ mol L$^{-1}$ KOH,, $1 \times 10^{-5}$ mol L$^{-1}$ EDTA, $1.2 \times 10^{-3}$ mol L$^{-1}$ $O_2$. Peroxide concn. $3 \times 10^{-3}$ mol L$^{-1}$. No reaction obs. | 84A909 |
| 261 | **Linolenate ion** | | | | | |
| | $O_2^- + L^- \rightarrow$ | alk. | $10^{-2}$–$10^{-1}$ | s.f., opt. | 85% v/v EtOH in 0.001–0.01 mol L$^{-1}$ KOH/$H_2O$, Anaerobic conditions. D.k. at 240–270 nm. Reaction negligible. | 83A087 |
| | | 11 | $<1$ | p.r., opt. | D.k. in soln. contg. 0.06 mol L$^{-1}$ formate and 0.01 mol L$^{-1}$ lipid. | 78A365 |
| 262 | **Linolenic acid** | | | | | |
| | $HO_2 + LH \rightarrow$ | | $(1.70 \pm 0.35) \times 10^3$ | s.f., opt. | 85% v/v ethanolic soln.; d.k. at 240–270 nm; 0.05 mol L$^{-1}$ $H_2SO_4$. | 83A087 |
| 263 | **Lipoxidase (soybean)** | | | | | |
| | $HO_2/O_2^- + LOX \rightarrow$ | 3.98 | $(7.0 \pm 1.0) \times 10^6$ | p.r., opt. | P.b.k. in $O_2$-satd. soln. contg. 0.1 mol L$^{-1}$ formate ion and $5 \times 10^{-6}$ mol L$^{-1}$ lipoxidase, product is Fe(III) yellow enzyme. | 80A296 |
| | $O_2^- + LOX \rightarrow$ | 9.3 | | p.r., opt. | P.b.k. in $O_2$-satd. soln. contg. 0.1 mol L$^{-1}$ formate ion. No reaction obs. | 80A296 |
| 264 | **Luminol radical** | | | | | |
| | $O_2^- + lum\cdot \rightarrow lumO_2H$ | 7.7<br>11 | $1.4 \times 10^9$<br>$2 \times 10^8$ | p.r., opt. | D.k. at 430 nm in soln. contg. $10^{-4}$ mol L$^{-1}$ luminol and $10^{-1}$ mol L$^{-1}$ $H_2O_2$; p$K_a$ for luminol hydroperoxide detd. to be $9.3 \pm 0.3$; pH range of 7.7–11.0 studied. | 80A221 |
| 265 | **DL-Lysine, p$K_a$ = 5.05, 10.53, 11.82** | | | | | |
| | $HO_2 + Lys \rightarrow$ | 1.4 | $<13.3 \pm 3.0$ | $\gamma$-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ lysine; upper limit. | 79A358 |
| | $O_2^- + Lys \rightarrow$ | 8.5 | $<3.30 \pm 0.03$ | $\gamma$-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ lysine; no reaction obs. | 79A358 |
| 266 | **L-Malate ion** | | | | | |
| | $O_2^- + {}^-O_2CCH_2CHOHCO_2^- \rightarrow$ | 10.1 | $<0.11$ | *e*-r., s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and $10^{-4}$ mol L$^{-1}$ EDTA and 0.01–0.1 mol L$^{-1}$ malate; no reaction obs. | 770046 |
| 267 | **Maleate ion** | | | | | |
| | $O_2^- +$ *cis*-$^-O_2CCH{=}CHCO_2^- \rightarrow$ | 10.0 | $<0.06$ | *e*-r., s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and $10^{-4}$ mol L$^{-1}$ EDTA and $10^{-4}$–$5 \times 10^{-2}$ mol L$^{-1}$ maleate; no reaction obs. | 770046 |
| 268 | **Methemoglobin** | | | | | |
| | $HO_2/O_2^- + Fe^{3+}Hb \rightarrow Fe^{2+}HbO_2$ | 7.8 | $1.4 \times 10^3$ | $\gamma$-r. | Rel. to $k(O_2^- + HO_2) = 8.5 \times 10^7$; soln. contg. 0.16 mol L$^{-1}$ formate and $O_2$. | 78A366 |
| | | | | p.r. | No reaction detected; pH not given. | 761137 |
| | | 7 | $6 \times 10^3$ | $\gamma$-r., enz. | Rel. to $O_2^- + Fe^{2+}$ $HbO_2$. | 763093 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 269 | **Methional** | | | | | |
| | $HO_2/O_2^-$ + $CH_3SCH_2CH_2CHO$ → | 7 | | p.r., opt. | D.k. at 240–260 nm; first order $k = 5.2 \times 10^3$ s$^{-1}$. Authors suggest sluggish reaction. | 761038 |
| 270 | **DL-Methionine, p$K_a$ = 2.2, 9.2** | | | | | |
| | $HO_2$ + Met → | 1.5 | <48.8 ± 15.0 | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and 5 × 10$^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ methionine; upper limit. | 79A358 |
| | $O_2^-$ + Met → | 8.3 | <0.33 ± 0.05 | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and 5 × 10$^{-5}$ mol L$^-$ EDTA and 0.1 mol L$^{-1}$ methionone; no reaction obs. | 79A358 |
| 271 | **4-Methoxyphenyl-*N*-*tert*-butylnitrone** | | | | | |
| | $HO_2/O_2^-$ + 4-$CH_3O$-PBN → $OH^-$ + 4-$CH_3O$-PBN(OOH) | | <1 × 10$^6$ | p.r., opt. | C.k. in $O_2$-satd. soln. contg. *tert*-BuOH or formate; obs. Q·$^-$ at 420 nm; rel. to $k(O_2^- + Q) = 1.0 \times 10^9$; See [80A176], limit seems high. | 82A184 |
| 272 | **Methyl-1,4-benzoquinone** | | | | | |
| | $O_2^-$ + MeQ → MeQ·$^-$ + $O_2$ | 7.0 | 8.0 × 10$^8$ | p.r., opt. | P.b.k. at 430 nm in soln. contg. 5 × 10$^{-5}$ mol L$^{-1}$ quinone. | 730068 |
| | | 7 | (7.6 ± 1) × 10$^8$ | p.r., opt. | P.b.k. (semiquinone) | 730125 |
| 273 | **3-Methylcholanthrene** | | | | | |
| | $HO_2/O_2^-$ + $C_{21}H_{16}$ → | | 1.1 × 10$^8$ | p.r. | C.k. in soln. contg. 0.01 mol L$^{-1}$ CTAB; rel. to $k(O_2^- + Q) = 9.5 \times 10^8$; pH not given. | 78A367 |
| 274 | **Methylhydroquinone** | | | | | |
| | $O_2^-$ + $CH_3C_6H_3$-1,4-$(OH)_2$ → MeQ·$^-$ + $H_2O_2$ | 7.0 | 1.7 × 10$^7$ | p.r. | Soln. cont. 10$^{-3}$ mol L$^{-1}$ $QH_2$. | 751011 |
| 275 | **1-Methylimidazole, p$K_a$ = 6.95** | | | | | |
| | $O_2^-$ + 1-$CH_3$Im → | 10.1 | <0.15 | *e*-r., s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and 10$^{-4}$ mol L$^{-1}$ EDTA and 0.01–0.1 mol L$^{-1}$ 1-methylimidazole; no reaction obs. | 770046 |
| 276 | **2-Methylimidazole, p$K_a$ = 6.95** | | | | | |
| | $O_2^-$ + 2-$CH_3$Im → | 10.1 | <0.18 | *e*-r., s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and 10$^{-4}$ mol L$^{-1}$ EDTA and 0.01–0.1 mol L$^{-1}$ 2-methylimidazole; no reaction obs. | 770046 |
| 277 | **2-Methyl-1,4-naphthoquinone** | | | | | |
| | $O_2^-$ + 2-$CH_3$-NQ → $O_2$ + 2-$CH_3$-NQ·$^-$ | 7 | 3.8 × 10$^7$ | p.r., opt. | D.k. of semiquinone. | 751090 |
| 278 | **4-Methylphenyl-*N*-*tert*-butylnitrone** | | | | | |
| | $HO_2/O_2^-$ + 4-$CH_3$-PBN → $OH^-$ + 4-$CH_3$-PBN(OOH) | | <1 × 10$^6$ | p.r., opt. | C.k. in $O_2$-satd. soln. contg. *tert*-BuOH or formate; obs. Q·$^-$ at 420 nm; rel. to $k(O_2^- + Q) = 1.0 \times 10^9$; See [80A176], limit seems high. | 82A184 |
| 279 | **Metmyoglobin** | | | | | |
| | $O_2^-$ + ferriMb → | | | p.r. | No reaction detected; pH not given. | 761137 |
| 280 | **NADH-Lactate dehydrogenase complex** | | | | | |
| | $HO_2$ + NADH-LDH → | 4.5–9 | ~2 × 10$^6$ | p.r. | Rate calcd. from pH study. | 763048 |
| | $O_2^-$ + NADH-LDH → | 7.5–9.0 | (1.0 ± 0.2) × 10$^5$ | p.r., opt. | D.k. of NADH (varying chain length) at 380 nm in air-satd. soln. contg. 0.1 mol L$^{-1}$ formate and 10$^{-4}$ mol L$^{-1}$ EDTA; pH 4.5–9.0 studied. | 763048 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 281 | **1,2-Naphthoquinone** | | | | | |
| | $O_2^- + 1,2\text{-NQ} \rightarrow 1,2\text{-NQ}^{\cdot -} + O_2$ | 7.0 | $7.2 \times 10^8$ | p.r., opt. | P.b.k. at 365 nm in soln. contg. $5 \times 10^{-6}$ mol L$^{-1}$ quinone. | 730068 |
| 282 | **1,2-Naphthoquinone-4-sulfonate ion** | | | | | |
| | $O_2^- + 4\text{-}SO_3NQ^- \rightarrow$ | 7.0 | $8.4 \times 10^8$ | p.r., opt. | P.b.k. at 365 nm in soln. contg. $5 \times 10^{-5}$ mol L$^{-1}$ quinone. | 730068 |
| 283 | **1,4-Naphthoquinone-2-sulfonate ion** | | | | | |
| | $O_2^- + 2\text{-}SO_3NQ^- \rightarrow$ $2\text{-}SO_3NQ^{\cdot 2-} + O_2$ | 7.0 | $6.6 \times 10^8$ | p.r., opt. | P.b.k. at 400 nm in soln. contg. $5 \times 10^{-5}$ mol L$^{-1}$ quinone. | 730068 |
| | | 6.8 | $(2.5 \pm 0.4) \times 10^8$ | p.r., opt. | P.b.k. at 402 nm (semiquinone) in soln. contg. 0.2 mol L$^{-1}$ glycine satd. with $N_2O/O_2$; same result with formate instead of glycine. | 761082 |
| 284 | **2-Naphthylamine** | | | | | |
| | $HO_2/O_2^- + 2\text{-}NpNH_2 \rightarrow$ | | $1.3 \times 10^7$ | p.r. | C.k.; rel. to $k(O_2^- + Q) = 9.5 \times 10^8$; pH not given. | 78A367 |
| 285 | **Nicotinamide adenine dinucleotide, reduced** | | | | | |
| | $HO_2 + NADH \rightarrow$ $H_2O_2 + [NAD]\cdot$ | 4.4–6.3 | $(1.8 \pm 0.2) \times 10^5$ | f.p., opt. | D.k. at 340 and 366 nm. Value calcd. from $k_{obs}$ vs pH study. Buffered with acetate or phosphate ($I = 0.03$). $O_2^-$ is unreactive. | 79A170 |
| | $HO_2/O_2^- + NADH \rightarrow$ $H_2O_2 + [NAD]\cdot$ | 5.1 | $<3.5 \times 10^4$ | elec., opt. | Opt. detection at 450 nm in soln. contg. 0.01 mol L$^{-1}$ acetate. | 78R209 |
| | $O_2^- + NADH \rightarrow$ $H_2O_2 + [NAD]\cdot$ | 8.6 | $\leqslant 27$ | X-r., biol. | Estd. in soln. contg. KBr and $O_2$. | 710158 |
| 286 | **Nitro Blue Tetrazolium** | | | | | |
| | $O_2^- + NBT^{2+} \rightarrow O_2 + NBT^{\cdot +}$ | 7–11 | $(5.88 \pm 0.12) \times 10^4$ | phot., s.f., opt. | P.b.k. at 530 nm in soln. contg. $5 \times 10^{-3}$ mol L$^{-1}$ formate and 0.25–1.25 $\times 10^{-3}$ mol L$^{-1}$ $O_2$ and $2 \times 10^{-5}$ mol L$^{-1}$ EDTA, mixed with 0.2 mol L$^{-1}$ phosphate soln. contg. (0.4–1.8) $\times 10^{-3}$ $NBT^{2+}$. | 80A085 |
| | | 9.8 | $5.94 \times 10^4$ | *e*-r., s.f., opt. | P.b.k. at 560 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and $2 \times 10^{-4}$ mol L$^{-1}$ EDTA and (0.2–1) $\times 10^{-3}$ mol L$^{-1}$ $NBT^{2+}$; cor. for $O_2^-$ decay. | 770046 |
| 287 | **4-Nitrophenyl-*N*-*tert*-butylnitrone** | | | | | |
| | $HO_2/O_2^- + 4\text{-}NO_2\text{-}PBN \rightarrow$ $OH^- + 4\text{-}NO_2\text{-}PBN(OOH)$ | | $<3 \times 10^6$ | p.r., opt. | C.k. in $O_2$-satd. soln. contg. *tert*-BuOH or formate; obs. $Q^{\cdot -}$ at 420 nm; rel. to $k(O_2^- + Q) = 1.0 \times 10^9$; See [80A176], limit seems high. | 82A184 |
| 288 | **9,11-Octadecadienoate ion** | | | | | |
| | $O_2^- + OD^- \rightarrow$ | alk. | $\leqslant 0.01$ | s.f., opt. | 85% v/v EtOH in 0.001–0.01 mol L$^{-1}$ KOH/$H_2O$. Anaerobic conditions. D.k. at 240–270 nm. Reaction negligible. Mixture with 10,12-octadecadienoate ion. | 83A087 |
| 289 | **9,11-Octadecadienoic acid** | | | | | |
| | $HO_2 + ODH \rightarrow$ | acid | | s.f., opt. | 85% v/v EtOH in 0.05 mol L$^{-1}$ $H_2SO_4/H_2O$. Anaerobic conditions. D.k. at 240–270 nm. Mixture with 10,12-isomer. No reaction obs. | 83A087 |
| 290 | **Oleate ion** | | | | | |
| | $O_2^- + OI^- \rightarrow$ | alk. | $\leqslant 0.01$ | s.f., opt. | 85% v/v EtOH in 0.001–0.01 mol L$^{-1}$ KOH/$H_2O$. Anaerobic conditions. D.k. at 240–270 nm. Reaction negligible. | 83A087 |
| 291 | **Oleic acid** | | | | | |
| | $HO_2 + OIH \rightarrow$ | acid | | s.f., opt. | No reaction obs.; 85% v/v ethanolic soln.; d.k. at 240–270 nm; 0.05 mol L$^{-1}$ $H_2SO_4$. | 83A087 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 292 | **Oleic acid hydroperoxide** | | | | | |
| | $HO_2$ + $HO_2$-OlH → | acid | | s.f., opt. | D.k. at 250–270 nm in 80% EtOH soln. with $5 \times 10^{-2}$ mol L$^{-1}$ $H_2SO_4$, $1 \times 10^{-5}$ mol L$^{-1}$ EDTA, $1.2 \times 10^{-3}$ mol L$^{-1}$ $O_2$. Peroxide concn. $3.8 \times 10^{-2}$ mol L$^{-1}$. No reaction obs. | 84A909 |
| | $O_2^-$ + $HO_2$-Ol$^-$ → | alk. | | s.f., opt. | D.k. at 250–270 nm in 80% EtOH soln. with $10^{-2}$ mol L$^{-1}$ KOH,, $1 \times 10^{-5}$ mol L$^{-1}$ EDTA, $1.2 \times 10^{-3}$ mol L$^{-1}$ $O_2$. Peroxide concn. $3 \times 10^{-3}$ mol L$^{-1}$. No reaction obs. | 84A909 |
| 293 | **Oxalate ion** | | | | | |
| | $O_2^-$ + $^-O_2CCO_2^-$ → | 10.0 | <0.20 | *e*-r., s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and $10^{-4}$ mol L$^{-1}$ EDTA and (5–50) $\times 10^{-3}$ mol L$^{-1}$ oxalate; no reaction obs. | 770046 |
| 294 | **2-Oxoglutarate ion** | | | | | |
| | $O_2^-$ + $^-O_2CCH_2CH_2COCO_2^-$ → | 10.1 | <0.30 | *e*-r., s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and $10^{-4}$ mol L$^{-1}$ EDTA and 0.01–0.02 mol L$^{-1}$ 2-oxoglutarate; no reaction obs. | 770046 |
| 295 | **Oxyhemoglobin** | | | | | |
| | $HO_2/O_2^-$ + $Fe^{2+}$ $HbO_2$ → | 7.8 | $<5 \times 10^2$ | p.r., opt. | Obs. no change at 430 nm in soln. contg. $O_2$ and 0.16 mol L$^{-1}$ formate; $\gamma$-r. showed slight oxidation. | 78A366 |
| | | 7 | $(4 \pm 1) \times 10^3$ | $\gamma$-r., enz. | Obs. inhibition of SOD; rel. to $O_2^-$ + Methemoglobin. | 763093 |
| 296 | **Peroxidase Compound I** | | | | | |
| | $HO_2$ + HRP Compound I → HRP Compound II | 3.8–8.8 | $2.2 \times 10^8$ | p.r., opt. | D.k.; calcd. value from pH study and curve fitting; soln cont. $4.7 \times 10^{-6}$ mol L$^{-1}$ Compound I, $1.5 \times 10^{-5}$ mol L$^{-1}$ peroxide, $2.5 \times 10^{-4}$ mol L$^{-1}$ $O_2$, as well as phosphate and formate. | 741148 |
| | $O_2^-$ + HRP Compound I → HRP Compound II | 7.2–8.8 | $1.6 \times 10^6$ | p.r., opt. | D.k. as well as p.b.k. | 741148 |
| 297 | **Peroxidase (horseradish)** | | | | | |
| | $HO_2/O_2^-$ + HRP → | 5.1 | $1.5 \times 10^5$ | elec., opt. | Opt. detection at 450 nm, 0.01 mol L$^{-1}$ acetate. | 78R209 |
| | | 5.0 | $\sim 3.5 \times 10^8$ | enz., | Obs. formn. of oxyperoxidase at 418 nm in | 733173 |
| | | 5.5 | $\sim 2.5 \times 10^8$ | opt. | soln. contg. 0.1 mol L$^{-1}$ acetate, $1.5 \times 10^{-6}$ mol L$^{-1}$ $H_2O_2$, $10^{-4}$ mol L$^{-1}$ NADH, $8.4 \times 10^{-6}$ mol L$^{-1}$ HRP and $0.64–13 \times 10^{-6}$ mol L$^{-1}$ SOD. Rel. to $k(O_2^-$ + SOD). | |
| 298 | **Peroxyhydrothymine radical** | | | | | |
| | $HO_2/O_2^-$ + 5-$MeUO_2$· → $O_2$ + 5-$MeUO_2H$ | | $\sim 6 \times 10^6$ | p.r., opt. | D.k. at 270 nm in oxygenated soln. contg. dihydrothymine; hydroperoxide formn. occurs at about the same rate as the second order decay of the peroxy radical; pH not given. | 741151 |
| 299 | **L-Phenylalanine, p$K_a$ = 2.16, 9.1** | | | | | |
| | $HO_2$ + Phe → | 1.3 | $<180.0 \pm 50.0$ | $\gamma$-r., s.f., opt. | D.k. in $O_2$—satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ phenylalanine; upper limit. | 79A358 |
| | $O_2^-$ + Phe → | 10.1 | $<0.36 \pm 0.05$ | phot. | C.k. with $NBT^{2+}$ in soln. contg. 0.043 mol L$^{-1}$ phenylalanine; no reaction obs. | 79A358 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 300 | **Phenyl-*N*-*tert*-butylnitrone** | | | | | |
| | $HO_2/O_2^-$ + PBN → $OH^-$ + PBN(OOH) | | $<1 \times 10^6$ | p.r., opt. | C.k. in $O_2$-satd. soln. contg. *tert*-BuOH or formate; obs. $Q\cdot^-$ at 420 nm; rel. to $k(O_2^- + Q) = 1.0 \times 10^9$; See [80A176], limit seems high. | 82A184 |
| 301 | **Phloroglucinol** | | | | | |
| | $HO_2$ + $C_6H_3(OH)_3$ → | 0.5–1.5 | $(2.3 \pm 0.3) \times 10^3$ | s.f., opt. | D.k. at 242 nm; soln. prepd. as in [83G122]. | 82Z254 |
| 302 | **Plastocyanin** | | | | | |
| | $HO_2/O_2^-$ + Plastocyanin → | 8.0 | $<10^6$ | p.r., opt. | No reaction obs. at 290 nm in $O_2$-satd. soln. contg. $2 \times 10^{-2}$ mol L$^{-1}$ Na formate. | 761021 |
| 303 | **L-Proline, p$K_a$ = 1.952, 10.640** | | | | | |
| | $HO_2$ + Pro → | 1.4 | $<17.3 \pm 3.0$ | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate ion and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ proline; upper limit. | 79A358 |
| | $O_2^-$ + Pro → | 10.0 | $<0.16 \pm 0.05$ | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate ion and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ proline; no reaction obs. | 79A358 |
| 304 | **Pyruvate ion** | | | | | |
| | $O_2^-$ + $CH_3COCO_2^-$ → | 10.0 | <0.10 | *e*-r., s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and $10^{-4}$ mol L$^{-1}$ EDTA and $(1–10) \times 10^{-3}$ mol L$^{-1}$ pyruvate; no reaction obs. | 770046 |
| 305 | **Resorcinol** | | | | | |
| | $HO_2$ + 1,3-$C_6H_4(OH)_2$ → | 0.5–1.5 | $(4.1 \pm 0.1) \times 10^3$ | s.f., opt. | D.k. at 242 nm; soln. prepd. as in [83G122]. | 82Z254 |
| | $O_2^-$ + 1,3-$C_6H_4(OH)_2$ → | 5.0–8.5 | $2.0 \pm 1$ | s.f., opt. | D.k. at 242 nm; soln. prepd. as in [83G122]. | 82Z254<br>83A902 |
| 306 | **Riboflavin semiquinone** | | | | | |
| | $O_2^-$ + RFH· → | 7 | $(7.1 \pm 0.2) \times 10^8$ | p.r., opt. | D.k. at 540 nm in aerated soln. contg. 0.01 mol L$^{-1}$ formate ion and $8 \times 10^{-5}$ mol L$^{-1}$ flavin. | 81A375 |
| 307 | **DL-Serine, p$K_a$ = 2.186, 9.208** | | | | | |
| | $HO_2$ + Ser → | 1.2 | $<54.6 \pm 8.0$ | γ-r., s.r., opt. | D.k. in $O_2$-satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ serine; upper limit. | 79A358 |
| | $O_2^-$ + Ser → | 9.0 | $<0.53 \pm 0.04$ | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ serine; no reaction. | 79A358 |
| 308 | **Succinate ion** | | | | | |
| | $O_2^-$ + $^-O_2CCH_2CH_2CO_2^-$ → | 9.9 | <0.25 | *e*-r., s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and 0.1 mol L$^{-1}$ EDTA and 0.01–0.1 mol L$^{-1}$ succinate; no reaction obs. | 770046 |
| 309 | **Sulfacetamide** | | | | | |
| | $HO_2/O_2^-$ + SA → | 6.5 | $7 \times 10^7$ | p.r., opt. | P.b.k. at 470 nm ($\epsilon_{470}$ = 155 L mol$^{-1}$ cm$^{-1}$) in $O_2$-satd. soln. contg. $10^{-1}$ mol L$^{-1}$ Na formate and $10^{-3}$ mol L$^{-1}$ substrate. | 82A138 |
| 310 | **Superoxide dismutase (Co,Co)** | | | | | |
| | $2\ O_2^- + 2\ H_2O \xrightarrow{SOD} H_2O_2 + O_2 + 2\ OH^-$ | 7.4<br>9.4 | $(1.9 \pm 0.3) \times 10^8$<br>$(1.5 \pm 0.2) \times 10^9$ | p.r., opt. | (Co,Co) protein. D.k. at 250 nm in presence of phosphate or pyrophosphate buffer and 0.1 mol L$^{-1}$ EtOH and $10^{-4}$ mol L$^{-1}$ EDTA; also obs. d.k. and p.b.k. at 575 nm (Co). Partial inhibition in presence of phosphate leading to $k \sim 1.9–2.3 \times 10^8$ at pH 9.4. | 82R132 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 311 | **Superoxide dismutase (Co,Zn)** $2\,O_2^- + 2\,H_2O \xrightarrow{SOD} H_2O_2 + O_2 + 2\,OH^-$ | 7.4 | $(2.3 \pm 0.3) \times 10^8$ | p.r., opt. | (Co,Zn) protein. D.k. at 250 nm in presence of phosphate or pyrophosphate buffer and 0.1 mol L$^{-1}$ EtOH and $10^{-4}$ mol L$^{-1}$ EDTA; also obs. d.k. and p.b.k. at 575 nm (Co). | 82R132 |
| | | 9.4 | $(1.6 \pm 0.2) \times 10^9$ | | | |
| 312 | **Superoxide dismutase (Cu,Co)** $2\,O_2^- + 2\,H_2O \xrightarrow{SOD} H_2O_2 + O_2 + 2\,OH^-$ | 9 | $(3.23 \pm 0.14) \times 10^9$ | p.r., opt. | (Cu,Co) protein. Soln. cont. 0.01 mol L$^{-1}$ EtOH, $2 \times 10^{-3}$ mol L$^{-1}$ Na pyrophosphate, $1 \times 10^{-4}$ mol L$^{-1}$ EDTA. | 77R237 |
| | | 7.4 | $(1.3 \pm 0.1) \times 10^9$ | p.r., opt. | D.k., Cu,Co enzyme. pH not varied but system shown previously to be independent of pH. | 75A243 |
| 313 | **Superoxide dismutase (Fe)** $2\,O_2^- + 2\,H_2O \xrightarrow{SOD} H_2O_2 + O_2 + 2\,OH^-$ | 8 | $5.5 \times 10^8$ | p.r., opt. | D.k. at 250 nm; SOD from marine bacterium (Fe-contg.); soln. contg. 0.1 mol L$^{-1}$ EtOH. Rate drops as pH increases. Second step as fast as first. | 771127 |
| | | 6.2–10.1 | $(6.1 \pm 1.3) \times 10^8$ | | | |
| 314 | **Superoxide dismutase (Mn)** $2\,O_2^- + 2\,H_2O \xrightarrow{SOD} H_2O_2 + O_2 + 2\,OH^-$ | 6.5 | $7.3 \times 10^8$ | p.r., opt. | D.k. at 250 nm; SOD from Bacillus stearothermophilus (Mn-contg.); soln. contg. EtOH and formate. Observed rate. | 77A231 |
| | | 10.2 | $1.2 \times 10^8$ | | | |
| | | 9.5 | $4 \times 10^8$ | | D.k. at 250 nm; $k = 7.5 \times 10^9$ for human SOD (Cu-Zn contg.); $k = 3 \times 10^9$ for bovine SOD (Cu-Zn contg.). Observed rate. | 769352 |
| | | 7.9 | $(1.3 \pm 0.15) \times 10^9$ | p.r., opt. | D.k. at 248 nm; E.coli Mn enzyme. Observed rate. | 743059 |
| 315 | **Superoxide dismutase** $2\,O_2^- + 2\,H_2O \xrightarrow{SOD} H_2O_2 + O_2 + 2\,OH^-$ | 7.3 | $1.75 \times 10^9$ | f.p., opt. | Effect of bovine liver SOD on reduction rate constant of cyt C; d.k. in soln. contg. $2 \times 10^{-2}$ mol L$^{-1}$ tetramethylethylenediamine, $10^{-5}$ mol L$^{-1}$ EDTA, $6 \times 10^{-5}$ mol L$^{-1}$ FMN and $\sim 10^{-5}$ mol L$^{-1}$ cyt C and SOD; d.k. without cyt C gave $k = 1.7 \times 10^9$. | 82A269 |
| | | 8.0 | $(5.37 \pm 0.42) \times 10^9$ | p.r., opt. | D.k. at 245 nm ($O_2^-$); phosphate buffer. | 82A448 |
| | | ~8 | $(1.3 \pm 0.1) \times 10^9$ | p.r., opt. | D.k. at 250 nm in soln. contg. $10^{-2}$ mol L$^{-1}$ formate. | 81A430 |
| | | 7.0 | $(2.6 \pm 0.3) \times 10^9$ | p.r., opt. | D.k. at 250 nm in oxygenated solution contg. $10^{-2}$ mol L$^{-1}$ formate. Observed rate. | 80A201 |
| | | 7.8 | $1.8 \times 10^9$ | p.r., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.1 mol L$^{-1}$ formate. Observed rate. | 80A220 |
| | | 7.0 | $3.0 \times 10^9$ | p.r., opt. | D.k. at 250 nm in oxygenated soln. contg. $3 \times 10^{-2}$ mol L$^{-1}$ formate and 2–4 $\times 10^{-7}$ mol L$^{-1}$ SOD; cor. for decay in absence of SOD; pH dependent (~4 to 7); reaction is interpreted to be $k(O_2^- + Cu^{II}) = k(O_2^- + Cu^{I}) = k(HO_2 + Cu^{II})$ and pH dependence due to conversion of SOD to inactive form by $H^+$. Observed rate. | 80A391 |
| | | 7.2 | $(1.6 \pm 0.64) \times 10^9$ | p.r., opt. | D.k.; protein from E. gracilis gave $k = (8.13 \pm 0.36) \times 10^9$. Observed rate. | 79R055 |
| | | 8.9 | $5.6 \times 10^8$ | p.r. | D.k. at 480 nm. Other rates detd. by data fitting with model. | 77A194 |
| | | 8–9 | $(3.70 \pm 0.18) \times 10^9$ | p.r., opt. | Soln. cont. $1 \times 10^{-4}$ mol L$^{-1}$ EDTA, 0.1 mol L$^{-1}$ EtOH, $5 \times 10^{-4}$ mol L$^{-1}$ sodium pyrophosphate; $k = (3.30 \pm 0.16) \times 10^9$ in soln. contg. $2 \times 10^{-3}$ mol L$^{-1}$ Na pyrophosphate and 0.085 mol L$^{-1}$ EtOH. | 77A275 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| | | 9 | $(3.15 \pm 0.14) \times 10^9$ | p.r., opt. | Soln. cont. 0.01 mol L$^{-1}$ EtOH, $2 \times 10^{-3}$ mol L$^{-1}$ Na pyrophosphate, $1 \times 10^{-4}$ mol L$^{-1}$ EDTA. | 77R237 |
| | | 7.2 | $(2.3 \pm 0.2) \times 10^9$ | p.r., opt. | Obs. decrease in transmittance at 550 nm ($Fe^{3+}$ cyt C), soln. also contains EDTA, phosphate buffer and formate; observed rate. | 761163 |
| | | 10.1 | $0.73 \times 10^9$ | $KO_2$, s.f., opt. | D.k. at 275 nm in soln. contg. borate and EDTA and bovine SOD contg. Cu. Observed rate. | 769257 |
| | | 7.5–7.7 | $(1.3 \pm 0.1) \times 10^9$ | p.r., opt. | D.k. at 245 nm in $O_2$-satd. soln. contg. formate ion $10^{-4}$ mol L$^{-1}$ EDTA and (1–5) $\times$ $10^{-6}$ mol L$^{-1}$ Cu,Zn enzyme; $k$ per equivalent of Cu; same result in presence of 0.11 g L$^{-1}$ bovine serum albumin. pH not varied but system shown previously to be independent of pH. | 75A243 |
| | | 9.0–9.9 | $(2.37 \pm 0.18) \times 10^9$ | p.r., opt. | D.k. at 250 nm; bovine Cu-Zn enzyme; supersedes [723066]. | 743017 |
| | | 9–10.2 | $2.3 \times 10^9$ | elec., pol. | Obs. increased $O_2$ formn. with enzyme addn. | 743132 |
| | | 7.5 | $(1.2 \pm 0.2) \times 10^9$ | p.r., opt. | D.k. at 650 nm; soln. contains Na formate and EDTA; enzyme from bovine blood. Observed rate. | 730109 |
| | | 5.0–9.5 | $\sim 2 \times 10^9$ | chem., biol., opt. | C.k. (bovine Cu-Zn enzyme); assume $k(O_2^- + \text{cyt C}) = 1.1 \times 10^5$ and $k(O_2^- + \text{TNM}) = 1.9 \times 10^9$; also detd. for Mn and Fe-contg. enzymes. | 733052 |
| | | 5.7–10.5 | $1.5 \times 10^9$ | p.r., opt. | D.k. at 690 nm; Cu enzyme from human blood. | 733132 |
| | | 7 | $(1.4 \pm 0.2) \times 10^9$ | p.r., opt. | D.k. at 245 nm; enzyme from bovine blood | 721007 |
| | | 4.8–9.5 | $2.3 \times 10^9$ | p.r., opt. | $k$ studied as a function of pH. | 723078 |
| 316 | **Tartrate ion** | | | | | |
| | $O_2^- + (CHOHCO_2^-)_2 \rightarrow$ | 10.1 | $<0.14$ | $e$-r., s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and $10^{-4}$ mol L$^{-1}$ EDTA and 0.01–0.1 mol L$^{-1}$ tartrate; no reaction. | 770046 |
| 317 | **1,1'-Tetramethylene-2,2'-bipyridinium radical ion (1+)** | | | | | |
| | $O_2^- + BP^{\cdot+} \rightarrow$ | 6.8 | $(13.0 \pm 1) \times 10^8$ | p.r. | Ar-satd. soln. cont. $10^{-3}$ mol L$^{-1}$ $BP^{2+}$ $2Cl^-$, 0.1 mol L$^{-1}$ Na formate and $\sim$0.3% $O_2$. | 78A321 |
| 318 | **2,2,6,6-Tetramethylpiperidine-*N*-oxyl** | | | | | |
| | $HO_2/O_2^- + \text{TEMPO} \rightarrow$ | 9.2 | 730 | | Calcd. rate. Soln. cont. 0.1 mol L$^{-1}$ borate, $2 \times 10^{-4}$ mol L$^{-1}$ EDTA, $10^{-7}$ mol L$^{-1}$ catalase; phosphate adjusted. | 79A184 |
| 319 | **2,2,6,6-Tetramethylpiperidin-1-ol** | | | | | |
| | $HO_2/O_2 + \text{TEMPOH} \rightarrow$ | 7.8 | $1.7 \times 10^3$ | enz., opt. | C.k. in xanthine oxidase system, rel. to $k(O_2^- + \text{cyt C})^- = 6 \times 10^5$. | 82R165 |
| 320 | **Tetranitromethane** | | | | | |
| | $HO_2 + C(NO_2)_4 \rightarrow NO_2 + H^+ + C(NO_2)_3^- + O_2$ | 0–6 | $< 10^5$ | p.r., opt. | P.b.k.; calcd. value from rate equation and pH study. | 650183 |
| | $O_2^- + C(NO_2)_4 \rightarrow NO_2 + C(NO_2)_3^- + O_2$ | 5.6–6.2 | $(1.9 \pm 0.4) \times 10^9$ | p.r., opt. | P.b.k.; pH 0–6.2 studied. | 650183 |
| | | | $(2.0 \pm 0.4) \times 10^9$ | p.r., opt. | P.b.k.; pH not given. | 640133 |
| 321 | **DL-Threonine, p$K_a$ = 2.088, 9.10** | | | | | |
| | $HO_2 + \text{Thr} \rightarrow$ | 1.4 | $<12.5 \pm 4.0$ | $\gamma$-r., s.f., opt. | D.k. in $O_2$-satd. formate soln. contg. $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ threonine; upper limit. | 79A358 |
| | $O_2^- + \text{Thr} \rightarrow$ | 10.1 | $<0.21 \pm 0.05$ | $\gamma$-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.15 mol L$^{-1}$ threonine; no reaction. | 79A358 |

TABLE 3. Rate constants for reactions of $HO_2/O_2^-$ in aqueous solutions — Continued

| No. | Reaction | pH | $k$ (L mol$^{-1}$s$^{-1}$) | Method | Comment | Ref. |
|---|---|---|---|---|---|---|
| 322 | **α-Tocopherol** | | | | | |
| | $HO_2 + C_{29}H_{50}O_2 \rightarrow$ | acid | $2.0 \times 10^5$ | s.f., opt. | Soln. cont. 0.022 mol L$^{-1}$ $H_2SO_4$, 85% EtOH, and 0.025–0.1 mol L$^{-1}$ α-tocopherol. | 82A403 |
| | $O_2^- + C_{29}H_{50}O_2 \rightarrow$ | alk. | | s.f., opt. | Soln. cont. 0.01 mol L$^{-1}$ KOH, 85% EtOH, and 0.025 –0.1 mol L$^{-1}$ α-tocopherol. No reaction obs. | 82A403 |
| 323 | **Tributylammoniobutyldioxy** | | | | | |
| | $O_2^- + (C_4H_9)_3N^+(O_2C_4H_8) \rightarrow O_3^-$ | ~12–13 | $6 \times 10^7$ | p.r., opt. | P.b.k. ($O_3^-$) in soln. contg. $O_2$, 0.1 mol L$^{-1}$ KOH and $R_4N^+$. Concn. of $O_2^-$ and cation varied. | 78A095 |
| 324 | **Triethylammonioethyldioxy** | | | | | |
| | $O_2^- + (C_2H_5)_3N^+(O_2CHCH_3) \rightarrow O_3^-$ | ~12–13 | $4 \times 10^8$ | p.r., opt. | P.b.k. ($O_3^-$) in soln. contg. $O_2$, 0.1 mol L$^{-1}$ KOH and $R_4N^+$. Concn. of $O_2^-$ and cation varied. | 78A095 |
| 325 | **Trimethylammoniomethyldioxy** | | | | | |
| | $O_2^- + (CH_3)_3N^+(O_2CH_2) \rightarrow O_3^-$ | ~12–13 | $3 \times 10^8$ | p.r., opt. | P.b.k. ($O_3^-$) in soln. contg. $O_2$, 0.1 mol L$^{-1}$ KOH and $R_4N^+$. Concn. of $O_2^-$ and cation varied. | 78A095 |
| 326 | **1,1'-Trimethylene-2,2'-bipyridinium radical ion (1+)** | | | | | |
| | $O_2^- + BP^{\cdot+} \rightarrow$ | 6.8 | $(12.0 \pm 1) \times 10^8$ | p.r. | Ar-satd. soln. contg. $10^{-3}$ mol L$^{-1}$ $BP^{2+}$ $2Cl^-$ and 0.1 mol L$^{-1}$ formate and ~0.3% $O_2$. | 78A321 |
| 327 | **2,5,5-Trimethyl-1-pyrroline *N*-oxide** | | | | | |
| | $HO_2/O_2^- + TMPO \rightarrow$ | 7.8 | 7 | enz., esr | Spin trapping; c.k. with SOD; rel. to $k(O_2^- + Fe^{3+}$ cyt C) $= 6 \times 10^5$. | 80A176 |
| | | 8.1 | 1.44 | enz., esr | Spin trapping; rel. to $k(O_2^- + O_2^-) = 5.1 \times 10^4$. Xanthine-xanthine oxidase system. | 80A176 |
| 328 | **Tripropylammoniopropyldioxy** | | | | | |
| | $O_2^- + (C_3H_7)_3N^+(O_2C_3H_6) \rightarrow O_3^-$ | ~12–13 | $8 \times 10^7$ | p.r., opt. | P.b.k. ($O_3^-$) in soln. contg. $O_2$, 0.1 mol L$^{-1}$ KOH and $R_4N^+$. Concn. of $O_2^-$ and cation varied. | 78A095 |
| 329 | **Tris(hydroxymethyl)aminomethane** | | | | | |
| | $O_2^- + (HOCH_2)_3CNH_2 \rightarrow$ | 10.1 | <0.001 | s.f., opt. | D.k. at 250 nm in air-satd. soln. contg. 0.2 mol L$^{-1}$ formate and $10^{-4}$ mol L$^{-1}$ EDTA and 0.01–0.1 mol L$^{-1}$ substrate; no reaction. | 770046 |
| 330 | **L-Tryptophan, p$K_a$ = 2.43, 9.44, 11.73** | | | | | |
| | $O_2^- + TrpH \rightarrow$ | 10.6 | $<24.0 \pm 3.00$ | phot., opt. | C.k. with $NBT^{2+}$; obs. at 560 nm in soln. contg. $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.02 mol L$^{-1}$ tryptophan; no reaction. | 79A358 |
| 331 | **L-Tyrosine, p$K_a$ = 2.2, 9.2, 10.5** | | | | | |
| | $O_2^- + TyrOH \rightarrow$ | 10.8 | $<10.00 \pm 2.00$ | phot., opt. | C.k. with $NBT^{2+}$; obs. at 560 nm in soln. contg. $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.005 mol L$^{-1}$ tyrosine; no reaction. | 79A358 |
| 332 | **DL-Valine, p$K_a$ = 2.3, 9.7** | | | | | |
| | $HO_2 + Val \rightarrow$ | 1.5 | $<10.5 \pm 1.3$ | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.1 mol L$^{-1}$ valine; upper limit. | 79A358 |
| | $O_2^- + Val \rightarrow$ | 10.1 | $<0.18 \pm 0.02$ | γ-r., s.f., opt. | D.k. in $O_2$-satd. soln. contg. formate and $5 \times 10^{-5}$ mol L$^{-1}$ EDTA and 0.15 mol L$^{-1}$ valine; no reaction obs. | 79A358 |
| 333 | **Vitamin $K_1$** | | | | | |
| | $HO_2/O_2^- + Me(phytyl)NQ \rightarrow Me(phytyl)NQ^{\cdot-} + O_2$ | 7 | $<2 \times 10^5$ | p.r., opt. | Detd. from equil. const. and d.k. of semiquinone. Soln. contg. 7 mol L$^{-1}$ 2-PrOH and 1 mol L$^{-1}$ acetone. | 730125 |

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## 10. Molecular Formula Index

$C_{16}H_{32}N_4Ni^{3+}$ 5,7,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienenickel(III) ion **139**

$C_{16}H_{35}NO_2^+$ Tributylammoniobutyldioxy **323**

$C_{16}H_{36}CoN_4O_2^{2+}$ Diaqua(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)cobalt(II) ion **21**

$C_{16}H_{36}CuN_4O_2^{2+}$ Diaqua(5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)copper(II) ion **38**

$C_{16}H_{36}N_4Ni^{2+}$ 5,7,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane-nickel(II) ion **134**

$C_{16}H_{36}N_4Ni^{3+}$ 5,7,7,12,12,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane-nickel(III) ion **138**

$C_{17}H_{21}N_2O_6$ Riboflavin semiquinone **306**

$C_{18}H_{14}CuO_8$ Bis(acetylsalicylato)copper(II) **71**

$C_{18}H_{20}CuN_2O_6$ Bis(tyrosinato)copper(II) **65**

$C_{18}H_{27}O_2^-$ Arachidonate ion **172**

$C_{18}H_{29}O_2^-$ Linolenate ion **261**

$C_{18}H_{30}O_2$ Linolenic acid **262**

$C_{18}H_{31}O_2$ Linoleate ion **258**
9,11-Octadecadienoate ion **288**

$C_{18}H_{32}O_2$ Linoleic acid **259**
9,11-Octadecadienoic acid **289**

$C_{18}H_{33}O_2^-$ Oleate ion **290**

$C_{18}H_{33}O_4^-$ Linoleate hydroperoxide **257**

$C_{18}H_{34}O_2$ Oleic acid **291**

$C_{18}H_{34}O_4$ Linoleic acid hydroperoxide **260**

$C_{18}H_{36}O_4$ Oleic acid hydroperoxide **292**

$C_{19}H_{16}ClNO_4$ Indomethacin **252**

$C_{20}H_{12}$ Benzo[*a*]pyrene **181**

$C_{20}H_{16}CoN_4^{2+}$ Bis(2,2'-bipyridine)cobalt(II) ion **19**

$C_{20}H_{32}O_2$ Arachidonic acid **173**

$C_{21}H_{16}$ 3-Methylcholanthrene **273**

$C_{21}H_{29}N_7O_{14}P$ Nicotinamide adenine dinucleotide, reduced **285**

$C_{22}H_{18}N_2^+$ 1,1'-Diphenyl-4,4'-bipyridinium radical ion (1+) **222**

$C_{24}H_{16}CuN_4^+$ Bis(1,10-phenanthroline)copper(I) ion **32**

$C_{24}H_{16}CuN_4^{2+}$ Bis(1,10-phenanthroline)copper(II) ion **39**

$C_{25}H_{48}N_6O_8$ Desferrioxamine B **108**

$C_{26}H_{34}CuO_6$ Bis(diisopropylsalicylato)copper(II) **70**

$C_{27}H_{33}N_9O_5P_2$ Flavin mononucleotide semiquinone **231**

$C_{28}H_{46}CuN_{10}O_8^{2-}$ Bis(glycylhistidylleucinato)-cuprate(II) ion **54**

$C_{29}H_{34}CuN_8Zn^{3+}$ Copper(2-[2-(pyridyl)ethylimino-methyl]pyridine) zinc(2-[2-(pyridyl)ethyliminomethyl]-pyridine) imidazole bridged complex **74**

$C_{29}H_{34}Cu_2N_8^{3+}$ Bis[copper(2-[2-(pyridyl)ethyl-iminomethyl]pyridine)]imidazole bridged complex **73**

$C_{29}H_{50}O_2$ α-Tocopherol **322**

$C_{30}H_{24}N_6Ru^{3+}$ Tris(2,2'-bipyridine)ruthenium(III) ion **149**

$C_{31}H_{46}O_2$ Vitamin $K_1$ **333**

$C_{33}H_{34}N_4O_6$ Biliverdin **184**

$C_{33}H_{36}N_4O_6$ Bilirubin **183**

$C_{34}H_{32}ClFeN_4O_4$ Hemin **109**

$C_{36}H_{24}FeN_6^{2+}$ Tris(1,10-phenanthroline)iron(II) ion **78**

$C_{40}H_{30}N_{10}O_6^{2+}$ Nitro Blue Tetrazolium **286**

$C_{40}H_{40}ClFeN_8O_4$ Hemin-diimidazole complex **110**

$C_{44}H_{24}CoN_4O_{12}S_4^{3-}$ Tetrakis(*p*-sulfonatophenyl)-porphinatocobaltate(III) ion **27**

$C_{44}H_{24}CuN_4O_{12}S_4^{4-}$ Tetrakis(*p*-sulfonatophenyl)-porphinatocuprate(II) ion **42**

$C_{44}H_{24}FeN_4O_{12}S_4^{3-}$ Tetrakis(*p*-sulfonatophenyl)-porphineferrate(III) ion **98**

$C_{44}H_{24}MnN_4O_{12}S_4^{3-}$ Tetrakis(*p*-sulfonatophenyl)-porphinatomanganate(III) ion **124**

$C_{44}H_{24}N_4NiO_{12}S_4^{4-}$ Tetrakis(*p*-sulfonatophenyl)-porphinatonickelate(II) ion **137**

$C_{44}H_{24}N_4O_{12}S_4Zn^{4-}$ Tetrakis(*p*-sulfonatophenyl)-porphinatozincate(II) ion **162**

$C_{44}H_{36}CoN_8^{5+}$ Tetrakis(4-*N*-methylpyridyl)-porphinecobalt(III) ion **26**

$C_{44}H_{36}CuN_8^{4+}$ Tetrakis(4-*N*-methylpyridyl)-porphinecopper(II) ion **40**

$C_{44}H_{36}FeN_8^{2+}$ Tetrakis(4-*N*-methylpyridyl)-porphineiron(III) ion **92**

$C_{44}H_{36}FeN_8O_2^{4+}$ Tetrakis(4-*N*-methylpyridyl)-porphineiron(III)-superoxide complex **93**

$C_{44}H_{36}MnN_8^{5+}$ Tetrakis(4-*N*-methylpyridyl)-porphinemanganese(III) ion **122**

$C_{44}H_{36}N_8Ni^{4+}$ Tetrakis(4-*N*-methylpyridyl)-porphinenickel(II) ion **135**

$C_{44}H_{36}N_8Zn^{4+}$ Tetrakis(4-*N*-methylpyridyl)-porphinatezinc(II) ion **160**

$C_{44}H_{64}O_{24}$ Crocin **192**

$C_{46}H_{36}FeN_{10}^{2+}$ Dicyanotetrakis(4-*N*-methyl-pyridyl)porphineiron(II) ion **80**

$C_{46}H_{36}FeN_{10}^{3+}$ Dicyanotetrakis(4-*N*-methyl-pyridyl)porphineiron(III) ion **94**

$C_{48}H_{32}FeN_4^{2+}$ Bis(4,7-diphenyl-1,10-phenanth-roline)iron(II) ion **79**

$C_{48}H_{32}FeN_4^{3+}$ Bis(4,7-diphenyl-1,10-phenanth-roline)iron(III) ion **91**

$C_{50}H_{32}FeN_8O_{12}S_4^{3-}$ Tetrakis(*p*-sulfonatophenyl)-porphineferrate(III)-diimidazole complex **99**

$C_{50}H_{44}FeN_{12}^{4+}$ Tetrakis(4-*N*-methylpyridyl)-porphineiron(II)-diimidazole complex **81**

$C_{50}H_{44}FeN_{12}^{5+}$ Tetrakis(4-*N*-methylpyridyl)-porphineiron(III)-diimidazole complex **95**

$C_{56}H_{54}FeN_{14}O_4^{4+}$ Tetrakis(4-*N*-methylpyridyl)-porphineiron(II)-dihistidine complex **82**

| | |
|---|---|
| $C_{56}H_{54}FeN_{14}O_4^{5+}$ | Tetrakis(4-*N*-methylpyridyl)-porphineiron(III)-dihistidine complex **96** |
| $C_{56}H_{60}CuN_8^{4+}$ | Tetrakis-4-(*N*,*N*,*N*-trimethyl-ammonio)phenylporphine-copper(II) ion **41** |
| $C_{56}H_{60}FeN_8^{5+}$ | Tetrakis-4-(*N*,*N*,*N*-trimethyl-ammonio)phenylporphine-iron(III) ion **97** |
| $C_{56}H_{60}MnN_8^{5+}$ | Tetrakis-4-(*N*,*N*,*N*-trimethyl-ammonio)phenylporphine-manganese(III) ion **123** |
| $C_{56}H_{60}N_8Ni^{4+}$ | Tetrakis-4-(*N*,*N*,*N*-trimethyl-ammonio)phenylporphine-nickel(II) ion **136** |
| $C_{56}H_{60}N_8Zn^{4+}$ | Tetrakis-4-(*N*,*N*,*N*-trimethyl-ammonio)phenylporphinezinc(II) ion **161** |
| $C_{63}H_{90}CoN_{14}O_{14}P$ | Cyanocob(III)alamin **30** |
| $C_{76}H_{60}Cl_4Cu_2N_4O_{16}$ | Copper indomethacin **76** |
| $Ce^{4+}$ | Cerium(IV) ion **10** |
| $Cl^-$ | Chloride ion **11** |
| ClHO | Hypochlorous acid **14** |
| $ClO_2$ | Chlorine dioxide **16** |
| $ClO_2^-$ | Chlorite ion **15** |
| $ClO_3^-$ | Chlorate ion **17** |
| $ClO_4^-$ | Perchlorate ion **18** |
| $Cl_2$ | Chlorine **13** |
| $Cl_2^-$ | Dichlorine radical ion **12** |
| $Cu^+$ | Copper(I) ion **31** |
| $Cu^{2+}$ | Copper(II) ion **33** |
| $CuH_3N^{2+}$ | Amminecopper(II) ion **34** |
| $CuH_6N_2^{2+}$ | Bisamminecopper(II) ion **35** |
| $CuH_9N_3^{2+}$ | Trisamminecopper(II) ion **36** |
| $CuH_{12}N_4^{2+}$ | Tetraamminecopper(II) ion **37** |
| $Fe^{2+}$ | Iron(II) ion **77** |
| $Fe^{3+}$ | Iron(III) ion **90** |
| $H^+$ | Hydrogen ion **113** |
| HO | Hydroxyl **141** |
| $HO_2^-$ | Hydroperoxide ion **144** |
| $HO_2Th^{4+}$ | Thorium(IV)-hydroperoxy complex **155** |
| $HO_4U^{2+}$ | Dioxouranium(VI)-hydroperoxy complex **158** |
| $H_2$ | Hydrogen **112** |
| $H_2O_2$ | Hydrogen peroxide **143** |
| $H_3NO$ | Hydroxylamine **131** |
| $I_2$ | Iodine **114** |
| $I_3^-$ | Triiodine ion **115** |
| $Mn^{2+}$ | Manganese(II) ion **116** |
| $MnO_4^-$ | Permanganate ion **127** |
| $MnO_4S$ | Manganese(II) sulfate **118** |
| $Mn_2O_7P_2$ | Manganese(II) pyrophosphate **117** |
| $NO_2$ | Nitrogen dioxide **132** |
| $NO_2^-$ | Nitrite ion **133** |
| $N_3$ | Azide radical **130** |
| $O^-$ | Oxygen ion(1−) **142** |
| $O_2U^{2+}$ | Uranyl(VI) ion **157** |
| $O_3$ | Ozone **145** |
| $O_3S^{2-}$ | Sulfite ion **151** |
| $O_3Te^{2-}$ | Tellurate(IV) ion **153** |
| $O_3V^+$ | Oxoperoxyvanadium(IV) ion **159** |
| $O_4Os$ | Osmium tetroxide **146** |
| $S^{2-}$ | Sulfide ion **150** |
| $Th^{4+}$ | Thorium(IV) ion **154** |
| $Tl^{2+}$ | Thallium(II) ion **156** |

## 11. Compound Name Index