

## 81. Solvent Isotope Effect on the Rate Constants of Singlet-Oxygen Quenching by edta and Its Metal Complexes

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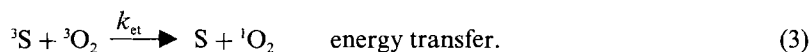
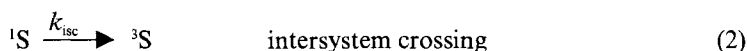
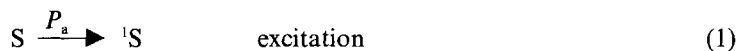
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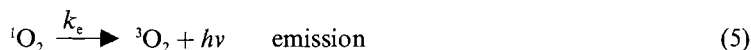
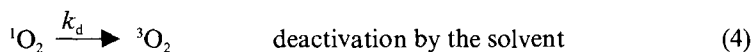
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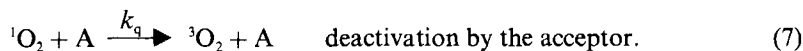
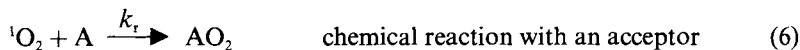
The reactivity of singlet oxygen ( $O_2(^1\Delta_g)$ ) with edta and its metal complexes with  $Al^{3+}$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ , and  $Mn^{2+}$  was investigated. The emission of singlet oxygen at 1270 nm in  $D_2O$  was measured in order to determine the quenching efficiency of edta and edta-metal complexes for different metal/edta ratios. The sum of the rate constants ( $k_r + k_q$ ) of the chemical reaction between singlet oxygen and the acceptor ( $k_r$ ) and of the physical quenching of singlet oxygen by the acceptor ( $k_q$ ) was obtained by a *Stern-Volmer* analysis. Measurements of the oxygen consumption in  $H_2O$  were used to determine quantum yields of the sensitized photooxidation, and the combined results of these experiments allowed the determination of  $k_r$  and  $k_q$  separately. A strong isotope effect was observed between the deuterated and the hydrogenated solvents. This effect was shown to be independent of the analytical procedure used. The isotope effect, as well as the reactivity of edta and its metal complexes, depend markedly on the complexed metal ion.

**1. Introduction.** – Because of its high capacity to form metal complexes, edta (ethylenediaminetetraacetic acid) is widely used *e.g.* in textile, photo, and galvano techniques. Consequently, edta and its metal complexes are also found in natural waters [1]. The elimination of these chelates is problematic due to their low adsorbability on sewage sludge and their poor biodegradability [2]. In addition, their oxidation with chlorine and chlorine dioxide was shown to be inefficient [3]. However, a decrease of the edta concentration was obtained through oxidation with  $O_3$  [3]. We were interested in investigating the reactivity of singlet oxygen  $O_2(^1\Delta_g)$  (denoted  $^1O_2$ ) with edta and its complexes with  $Fe^{3+}$ ,  $Cu^{2+}$ ,  $Mn^{2+}$ , and  $Al^{3+}$ . Singlet oxygen was produced by sensitization involving the electronic energy transfer from the triplet state of a sensitizer ( $^3S$ ) to molecular oxygen in its triplet ground state ( $^3O_2$ )



Chemical reaction and deactivation processes of  $^1O_2$  in solution can be represented by the following reactions





Several methods for evaluating and quantifying the reactivity of  ${}^1\text{O}_2$  are available, among them, the direct analysis by its luminescence at 1270 nm (see *e.g.* [4–6]) and the indirect analysis by making use of specific  ${}^1\text{O}_2$  acceptors [7].

**2. Results.** – 2.1. *Singlet-Oxygen Luminescence.* The luminescence of  ${}^1\text{O}_2$  at 1270 nm was measured with a Ge photodiode upon continuous excitation of the added sensitizer (S = Rose Bengal). A *Stern-Volmer* analysis of the quenching of  ${}^1\text{O}_2$  luminescence by an acceptor A permits the evaluation of the sum  $(k_r + k_q)$  [8].

In the absence of a  ${}^1\text{O}_2$  acceptor, and if the quenching of  ${}^1\text{O}_2$  by the sensitizer is negligible compared with the quenching by the solvent, the quantum yield of luminescence  $\Phi_e^0$  can be written as

$$\Phi_e^0 = \Phi_d^0 \cdot \frac{k_e}{k_e + k_d} \quad (8)$$

where  $\Phi_d^0$  is the quantum yield of  ${}^1\text{O}_2$  production by the sensitizer;  $k_e$  and  $k_d$  are, respectively, the radiative and the nonradiative rate constants of  ${}^1\text{O}_2$  deactivation in the solvent used (*Eqns.* 5 and 4).

If a  ${}^1\text{O}_2$  acceptor is added to the solution,  $\Phi_e$ , at the beginning of the irradiation, is given by

$$\Phi_e = \Phi_d^0 \cdot \frac{k_e}{k_e + k_d + (k_r + k_q)[\text{A}]} \quad (9)$$

where  $k_r$  and  $k_q$  are the bimolecular rate constants of the chemical reaction between  ${}^1\text{O}_2$  and A (*Eqn.* 6), and of the physical quenching of  ${}^1\text{O}_2$  by A (*Eqn.* 7), respectively.

If the rate of quenching of the triplet state of the sensitizer by A



is negligible in comparison with the rate of energy transfer from this same triplet state to oxygen (*Eqn.* 3), then

$$\Phi_d = \Phi_d^0 \quad (11)$$

In this case, a *Stern-Volmer* analysis of the quenching of the  ${}^1\text{O}_2$  emission leads to a linear relationship between the ratio of the luminescence signals in the absence and in the presence of acceptor ( $I_0/I$ ) and the concentration of the acceptor

$$\frac{I_0}{I} = 1 + (k_r + k_q) \cdot \tau_d \cdot [\text{A}] = \frac{\Phi_e^0}{\Phi_e} \quad (12)$$

where  $\tau_d = 1/(k_e + k_d)$  is the  ${}^1\text{O}_2$  lifetime in the solvent used ( $\text{D}_2\text{O}$  in our experiments), in the absence of acceptor. If  $\tau_d$  is known, the sum  $k_t = k_r + k_q$  can be calculated from the slope of  $I_0/I = f([\text{A}])$ .

To obtain signals of suitable significance, the  ${}^1\text{O}_2$  luminescence was measured in  $\text{D}_2\text{O}$  where the  ${}^1\text{O}_2$  lifetime  $\tau_d$  is longer than in  $\text{H}_2\text{O}$  ( $\tau_d^{\text{D}_2\text{O}} = 60 \mu\text{s}$  [9–11];  $\tau_d^{\text{H}_2\text{O}} = 3.6 \mu\text{s}$  [9] [12]).

The quenching of the  ${}^1\text{O}_2$  luminescence was measured for edta and for its complexes at the following metal/edta ratios:  $\text{Al}^{3+}/\text{edta} = 1:2$ ,  $\text{Mn}^{2+}/\text{edta} = 1:2$ ,  $\text{Cu}^{2+}/\text{edta} = 1:2$ , and

1:10,  $\text{Fe}^{3+}/\text{edta} = 1:1$ , 1:2, and 1:10. In the presence of an excess of metal ions, edta forms 1:1 complexes. The edta complexes investigated show very high stability constants  $K_s$  ( $6 \cdot 10^{13}$  to  $10^{25} \text{ l mol}^{-1}$ ) [13]. Therefore, we can assume that, for a solution containing an excess of edta, the complex concentration is equal to the metal concentration in the solution.

In the absence of the investigated acceptors, the  $^1\text{O}_2$  emission signals are stable upon irradiation. However, in their presence the signals decrease indicating that a chemical reaction between  $^1\text{O}_2$  and edta or its metal complexes is taking place. For the *Stern-Volmer* analysis, the intensities of the signals were measured at the beginning of the irradiation, and at least two different samples were prepared for each concentration of acceptor.

A value of  $6.5 (\pm 0.7) \cdot 10^5 \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  for  $k_i^{\text{ED}}$  was calculated from the slope of the plot of  $I_0/I = f([\text{edta}])$  indicating a rather low reactivity of  $^1\text{O}_2$  with edta.

In the case of the metal complexes at different metal/edta ratios, the relative emission intensities ( $I_0/I$ ) were plotted against the complex (ME) concentrations. The measured signals comprise the influence of both, free edta ( $[\text{ED}_f]$ ) and the complex (ME), and the *Stern-Volmer* relation is given by

$$\frac{I_0}{I} = 1 + \tau_d \cdot (k_i^{\text{ED}} [\text{ED}_f] + k_i^{\text{ME}} [\text{ME}]) \quad (13)$$

where  $k_i^{\text{ED}}$  and  $k_i^{\text{ME}}$  represent the sums ( $k_t + k_q$ ) for edta and for the investigated complex, respectively. To determine  $k_i^{\text{ME}}$ , the free edta concentration ( $[\text{ED}_f]$ ) has to be expressed as a function of the total edta concentration ( $[\text{ED}_t]$ ) and of the complex concentration ( $[\text{ME}]$ )

$$[\text{ED}_f] = [\text{ED}_t] - [\text{ME}] \quad (14)$$

For a solution with a metal to edta ratio a/b

$$[\text{ED}_t] = \frac{b}{a} [\text{ME}] \quad (15)$$

and, therefore,

$$[\text{ED}_f] = \left( \frac{b}{a} - 1 \right) [\text{ME}] \quad (16)$$

Substituting Eqn. 16 in Eqn. 13, we obtain

$$\frac{I_0}{I} = 1 + \tau_d \cdot \left\{ \left( \frac{b}{a} - 1 \right) k_i^{\text{ED}} + k_i^{\text{ME}} \right\} [\text{ME}] \quad (17)$$

and, hence, for a 1:10 metal edta ratio

$$\frac{I_0}{I} = 1 + \tau_d \cdot (9k_i^{\text{ED}} + k_i^{\text{ME}}) [\text{ME}] \quad (18)$$

for a 1:2 metal/edta ratio

$$\frac{I_0}{I} = 1 + \tau_d \cdot (k_i^{\text{ED}} + k_i^{\text{ME}}) [\text{ME}] \quad (19)$$

and for a 1:1 metal/edta ratio

$$\frac{I_0}{I} = 1 + \tau_d \cdot k_i^{\text{ME}} [\text{ME}] \quad (20)$$

As  $k_t^{\text{ED}}$  was obtained from luminescence measurements with edta in the absence of metal ( $k_t^{\text{ED}} = 6.5(\pm 0.7) \cdot 10^5 \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ , see above),  $k_t^{\text{ME}}$  can be calculated (Eqn. 17). The values of  $\{(b/a - 1)k_t^{\text{ED}} + k_t^{\text{ME}}\}$  obtained from the slope of  $I_0/I = f([\text{ME}])$  and the calculated values of  $k_t^{\text{ME}}$  are listed in Table 1 for the different metal/edta ratios.

Table 1. Rate Constants  $k_t$  of the  $^1\text{O}_2$  Quenching by edta and Its Metal Complexes at Different Metal/edta Ratios (Solutions in  $\text{D}_2\text{O}$ )

	$(b/a - 1)k_t^{\text{ED}} + k_t^{\text{ME a)}$ [ $\text{l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ]	$k_t^{\text{ME}}$ [ $\text{l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ]		$(b/a - 1)k_t^{\text{ED}} + k_t^{\text{ME a)}$ [ $\text{l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ]	$k_t^{\text{ME}}$ [ $\text{l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ]
edta		$6.5(\pm 0.7) \cdot 10^5$ <sup>b)</sup>	$\text{Cu}^{2+}/\text{edta}$ (1:2)	$3.0(\pm 0.3) \cdot 10^7$	$2.9(\pm 0.3) \cdot 10^7$
$\text{Mn}^{2+}/\text{edta}$ (1:2)	$1.2(\pm 0.6) \cdot 10^6$	$5.8(\pm 0.7) \cdot 10^5$	$\text{Fe}^{3+}/\text{edta}$ (1:10)	$9.5(\pm 0.3) \cdot 10^7$	$8.9(\pm 0.3) \cdot 10^7$
$\text{Al}^{3+}/\text{edta}$ (1:2)	$7.9(\pm 0.6) \cdot 10^5$	$1.4(\pm 0.7) \cdot 10^5$	$\text{Fe}^{3+}/\text{edta}$ (1:2)	$9.2(\pm 0.4) \cdot 10^7$	$9.1(\pm 0.4) \cdot 10^7$
$\text{Cu}^{2+}/\text{edta}$ (1:10)	$3.5(\pm 0.6) \cdot 10^7$	$2.9(\pm 0.6) \cdot 10^7$	$\text{Fe}^{3+}/\text{edta}$ (1:1)	$9.0(\pm 0.7) \cdot 10^7$	$9.0(\pm 0.7) \cdot 10^7$

<sup>a)</sup> See Eqn. 17. <sup>b)</sup>  $k_t^{\text{ED}}$ .

The results show that the efficiency of  $^1\text{O}_2$  quenching depends strongly on the metal in the edta complex. edta and its complexes with  $\text{Al}^{3+}$  and  $\text{Mn}^{2+}$  are poor  $^1\text{O}_2$  quenchers. The value of the  $\text{Mn}^{2+}$  complex is, within the limits of experimental error, the same as of free edta. The  $k_t^{\text{ME}}$  value of the  $\text{Al}^{3+}$  complex is lower than  $k_t^{\text{ED}}$  of edta. The  $k_t^{\text{ME}}$  values of the  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  complexes are much higher than  $k_t^{\text{ED}}$ , the  $\text{Fe}^{3+}$  complex being a better  $^1\text{O}_2$  quencher than the  $\text{Cu}^{2+}$  complex. For both of these complexes,  $k_t^{\text{ME}}$  values remain independent of a variation of the metal to edta ratio and, hence, confirm our hypothesis that 1:1 complexes are formed at all investigated concentration ratios, and that the complex concentration is in fact equal to the metal concentration in the presence of an excess of edta.

2.2. Quantum Yields of Photooxidation. The quantum yields of oxygen disappearance

$$\Phi_{-\text{O}_2} = \frac{\Delta n_{\text{O}_2}}{P_{a,\lambda}} \quad (21)$$

were determined by combined measurements of oxygen consumption in a closed system and of the absorbed photon flux with an electronically integrating actinometer [14] [15]. Rose Bengal was used as a sensitizer. At low conversion (oxygen consumption  $\leq 10\%$ ), the reaction follows pseudo-zero-order kinetics, and the decrease of the oxygen concentration as a function of irradiation time is linear.

According to Eqns. 4–7 and assuming that the stoichiometry of the reaction between  $^1\text{O}_2$  and the acceptor A is 1, the quantum yield of photooxidation ( $\Phi_{\text{AO}_2}$ ) can be written as

$$\Phi_{\text{AO}_2} = \Phi_{-\text{O}_2} = \Phi_d \cdot \frac{k_r [\text{A}]}{k_d + k_e + (k_r + k_q) [\text{A}]} \quad (22)$$

where  $\Phi_d$  represents the quantum yield of  $^1\text{O}_2$  production by the sensitizer.

The values of  $\Phi_{\text{AO}_2}$  have been determined at different acceptor concentrations, and the plot of  $1/\Phi_{\text{AO}_2}$  as a function of  $1/[\text{A}]$  gives a linear relationship with an intercept  $c$  and a slope  $d$

$$\frac{1}{\Phi_{\text{AO}_2}} = \underbrace{\frac{k_r + k_q}{\Phi_d \cdot k_r}}_c + \underbrace{\frac{k_d + k_e}{\Phi_d \cdot k_r}}_d \cdot \frac{1}{[\text{A}]} \quad (23)$$

Knowing  $\Phi_d = 0.75$  [16] and  $\tau_d = 3.6 \mu\text{s}$  in  $\text{H}_2\text{O}$  [9], the value of  $k_r$  could be calculated from the slope  $d$

$$k_r = \frac{1}{\tau_d \cdot d \cdot \Phi_d} \quad (24)$$

The values of  $k_r$  and  $c$  were used to calculate  $k_q$

$$k_q = k_r (c \cdot \Phi_d - 1) \quad (25)$$

Quantum yields of photooxidation  $\Phi_{\text{AO}_2}$  were determined for edta in both  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . The values of  $k_r^{\text{ED}}$  and  $k_q^{\text{ED}}$  and their sum  $k_r^{\text{ED}}$ , obtained from  $1/\Phi_{\text{AO}_2} = f(1/[\text{edta}])$ , are listed in Table 2. Both rate constants,  $k_r^{\text{ED}}$  and  $k_q^{\text{ED}}$ , show a strong solvent effect being higher in  $\text{H}_2\text{O}$  than in  $\text{D}_2\text{O}$ . The ratio of  $k_r^{\text{ED}}$  in  $\text{H}_2\text{O}$  to  $k_r^{\text{ED}}$  in  $\text{D}_2\text{O}$  is 3.6. The solvent effect is even stronger on  $k_q^{\text{ED}}$  with a  $k_q^{\text{H}_2\text{O}}/k_q^{\text{D}_2\text{O}}$  ratio of ca. 7.

Table 2. Rate Constants  $k_r^{\text{ED}}$  of the Reaction between  $^1\text{O}_2$  and edta,  $k_q^{\text{ED}}$  of the Physical Quenching of  $^1\text{O}_2$  by edta and Sum  $k_r^{\text{ED}}$  ( $= k_r^{\text{ED}} + k_q^{\text{ED}}$ ) in  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ . Values in  $[\text{l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}]$ .

	$k_r^{\text{ED}}$	$k_q^{\text{ED}}$	$k_r^{\text{ED}}$
edta ( $\text{D}_2\text{O}$ )	$1.3(\pm 0.1) \cdot 10^5$	$5.5(\pm 0.5) \cdot 10^5$	$6.8(\pm 0.5) \cdot 10^5$
edta ( $\text{H}_2\text{O}$ )	$4.6(\pm 0.3) \cdot 10^5$	$4.0(\pm 0.5) \cdot 10^6$	$4.5(\pm 0.5) \cdot 10^6$

The value of the sum  $k_r^{\text{ED}}$  ( $= k_r^{\text{ED}} + k_q^{\text{ED}} = 6.8 (\pm 0.5) \cdot 10^5 \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ) obtained from the determination of  $\Phi_{\text{AO}_2}$  in  $\text{D}_2\text{O}$  is, within the experimental error, identical to  $k_r^{\text{ED}}$  ( $= 6.5 (\pm 0.7) \cdot 10^5 \text{ l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ ) obtained from luminescence experiments. We may, therefore, assume that the two different experimental methods used for the determination of the kinetic parameters of the reaction are equivalent.

For edta and its metal complexes at different metal/edta ratios,  $1/\Phi_{\text{AO}_2}$  was plotted as a function of  $1/[\text{ME}]$ . As in the case of the  $^1\text{O}_2$  luminescence measurements, the results may be explained by a combination of the quenching by both edta and the complex.  $\Phi_{\text{AO}_2}$  is given by

$$\Phi_{\text{AO}_2} = \Phi_d \cdot \frac{k_r^{\text{ED}} [\text{ED}] + k_r^{\text{ME}} [\text{ME}]}{k_d + k_e + (k_r^{\text{ED}} [\text{ED}] + k_r^{\text{ME}} [\text{ME}])} \quad (26)$$

where  $k_r^{\text{ED}}$  and  $k_r^{\text{ME}}$  represent the sums of  $(k_r + k_q)$  as calculated from measurements of the oxygen consumption for free edta and the complexes, respectively.

Expressing the concentration of free edta in Eqn. 26 as a function of the complex concentration, one obtains for a metal/edta ratio of 1:10

$$\frac{1}{\Phi_{\text{AO}_2}} = \frac{9k_r^{\text{ED}} + k_r^{\text{ME}}}{\Phi_d \cdot (9k_r^{\text{ED}} + k_r^{\text{ME}})} + \frac{k_d + k_e}{\Phi_d \cdot (9k_r^{\text{ED}} + k_r^{\text{ME}})} \cdot \frac{1}{[\text{ME}]} \quad (27)$$

and for a 1:2 metal/edta ratio

$$\frac{1}{\Phi_{\text{AO}_2}} = \frac{k_r^{\text{ED}} + k_r^{\text{ME}}}{\Phi_d \cdot (k_r^{\text{ED}} + k_r^{\text{ME}})} + \frac{k_d + k_e}{\Phi_d \cdot (k_r^{\text{ED}} + k_r^{\text{ME}})} \cdot \frac{1}{[\text{ME}]} \quad (28)$$

From the slope  $c$  and the intercept  $d$  of the plot of  $1/\Phi_{\text{AO}_2} = f(1/[\text{ME}])$ , the following sums can be calculated

$$xk_r^{\text{ED}} + k_r^{\text{ME}} = \frac{k_d + k_c}{d \cdot \Phi_d} \quad (29)$$

$$xk_q^{\text{ED}} + k_q^{\text{ME}} = (xk_r^{\text{ED}} + k_r^{\text{ME}}) \cdot (c \cdot \Phi_d - 1) \quad (30)$$

where  $x = 1$  for a 1:2 and  $x = 9$  for a 1:10 metal/edta ratio, respectively. After subtraction of the values  $k_r^{\text{ED}}$  and  $k_q^{\text{ED}}$  obtained for free edta, the values of  $k_r^{\text{ME}}$  and  $k_q^{\text{ME}}$  for the different complexes may be calculated, and the results are summarized in *Table 3*.

Table 3. Values of  $(xk_r^{\text{ED}} + k_r^{\text{ME}})$  and  $(xk_q^{\text{ED}} + k_q^{\text{ME}})$  and Calculated Rate Constants  $k_r^{\text{ME}}$  and  $k_q^{\text{ME}}$  for the Different [metal (edta)] Complexes in  $\text{H}_2\text{O}$  (Eqns. 29 and 30). Values in  $[\text{l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}]$ .

	$xk_r^{\text{ED}} + k_r^{\text{ME}}$	$xk_q^{\text{ED}} + k_q^{\text{ME}}$	$k_r^{\text{ME}}$	$k_q^{\text{ME}}$
$\text{Mn}^{2+}/\text{edta}$ (1:2)	$1.1(\pm 0.1) \cdot 10^6$	$8.1(\pm 1.0) \cdot 10^6$	$6.1(\pm 1.0) \cdot 10^5$	$4.7(\pm 1.0) \cdot 10^6$
$\text{Al}^{3+}/\text{edta}$ (1:2)	$7.7(\pm 0.5) \cdot 10^5$	$1.9(\pm 0.5) \cdot 10^7$	$1.9(\pm 0.4) \cdot 10^5$	$1.5(\pm 0.5) \cdot 10^7$
$\text{Cu}^{2+}/\text{edta}$ (1:10)	$6.0(\pm 1.0) \cdot 10^6$	$2.4(\pm 1.0) \cdot 10^8$	$1.9(\pm 1.0) \cdot 10^6$	$2.0(\pm 1.0) \cdot 10^8$
$\text{Cu}^{2+}/\text{edta}$ (1:2)	$2.3(\pm 1.0) \cdot 10^6$	$3.8(\pm 2.0) \cdot 10^8$	$1.8(\pm 1.0) \cdot 10^6$	$3.7(\pm 2.0) \cdot 10^8$
$\text{Fe}^{3+}/\text{edta}$ (1:10)	$1.2(\pm 0.1) \cdot 10^7$	$6.3(\pm 0.5) \cdot 10^8$	$7.9(\pm 1.0) \cdot 10^6$	$6.3(\pm 0.5) \cdot 10^8$
$\text{Fe}^{3+}/\text{edta}$ (1:2)	$6.7(\pm 1.0) \cdot 10^6$	$7.6(\pm 1.5) \cdot 10^8$	$6.2(\pm 1.0) \cdot 10^6$	$7.6(\pm 1.5) \cdot 10^8$

The  $\text{Al}^{3+}$  complex is the only one showing a lower rate constant  $k_r^{\text{ME}}$  than edta ( $k_r^{\text{ED}}$ ). The  $k_r^{\text{ME}}$  value of the  $\text{Mn}^{2+}$  complex is, within experimental error, equal to  $k_r^{\text{ED}}$ . Both, the  $\text{Cu}^{2+}$  and the  $\text{Fe}^{3+}$  complexes exhibit much higher values of  $k_r^{\text{ME}}$  than free edta, the  $\text{Fe}^{3+}$  complex reacting faster than the  $\text{Cu}^{2+}$  complex.

For edta and the four metal complexes investigated, rate constants of physical quenching are higher than the corresponding rate constants of chemical reaction. Rate constants determined for the  $\text{Mn}^{2+}$  complex are about identical to these determined for edta alone. The other three metal complexes ( $\text{Cu}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{Fe}^{3+}$ ) show  $k_q^{\text{ME}}$  values higher than  $k_q^{\text{ED}}$  of edta. Whereas  $k_q^{\text{ME}}$  of the  $\text{Al}^{3+}$  complex is of the same order of magnitude than  $k_q^{\text{ED}}$  of edta,  $k_q^{\text{ME}}$  values of the  $\text{Fe}^{3+}$  and the  $\text{Cu}^{2+}$  complexes are two orders of magnitude higher, the first being always more reactive than the latter. The  $k_r^{\text{ME}}$  and  $k_q^{\text{ME}}$  values calculated from the experiments with the different metal/edta ratios are independent of these ratios, confirming 1:1 complexation.

**3. Discussion.** – The rate constants of the chemical reaction ( $k_r$ ) and of the physical quenching ( $k_q$ ) of  $^1\text{O}_2$  by edta and its metal complexes with  $\text{Al}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Fe}^{3+}$ , as

Table 4. Rate Constants  $k_t$ ,  $k_r$ ,  $k_q$ , and  $k_r$  of  $^1\text{O}_2$  Quenching by edta and Its Metal Complexes. Values in  $[\text{l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}]$ .  $k_t$  in  $\text{D}_2\text{O}$  from luminescence experiments;  $k_r$ ,  $k_q$ , and  $k_r$  in  $\text{H}_2\text{O}$  from  $\Phi_{\text{AO}_2}$  measurements, unless otherwise indicated.

	$k_t$	$k_r$	$k_q$	$k_r$
edta ( $\text{D}_2\text{O}$ )	$6.5(\pm 0.7) \cdot 10^5$	$1.3(\pm 0.1) \cdot 10^5$	$5.5(\pm 0.5) \cdot 10^5$	$6.8(\pm 0.5) \cdot 10^5$
edta ( $\text{H}_2\text{O}$ )		$4.6(\pm 0.3) \cdot 10^5$	$4.0(\pm 0.5) \cdot 10^6$	$4.5(\pm 0.5) \cdot 10^6$
$\text{Mn}^{2+}/\text{edta}$	$5.8(\pm 1.0) \cdot 10^5$	$6.1(\pm 0.5) \cdot 10^5$	$4.1(\pm 1.0) \cdot 10^6$	$4.7(\pm 1.0) \cdot 10^6$
$\text{Al}^{3+}/\text{edta}$	$1.4(\pm 0.6) \cdot 10^5$	$1.9(\pm 0.4) \cdot 10^5$	$1.5(\pm 0.5) \cdot 10^7$	$1.5(\pm 0.5) \cdot 10^7$
$\text{Cu}^{2+}/\text{edta}$	$2.9(\pm 0.6) \cdot 10^7$	$1.9(\pm 1.0) \cdot 10^6$	$2.8(\pm 1.5) \cdot 10^8$	$2.8(\pm 1.5) \cdot 10^8$
$\text{Fe}^{3+}/\text{edta}$	$9.1(\pm 0.7) \cdot 10^7$	$7.1(\pm 1.0) \cdot 10^6$	$6.9(\pm 1.5) \cdot 10^8$	$7.0(\pm 1.5) \cdot 10^8$

well as the corresponding sums  $k_t = k_r + k_q$  were determined.  $k_t$  was obtained in D<sub>2</sub>O by a Stern-Volmer analysis of the quenching of the <sup>1</sup>O<sub>2</sub> luminescence at 1270 nm.  $k_r$  and  $k_q$  were calculated from  $\Phi_{A_{O_2}}$  determinations in H<sub>2</sub>O. The values for  $k_r$ ,  $k_r$ ,  $k_q$ , and  $k_t$ , where  $k_t$  represents the sum ( $k_r + k_q$ ) of the rate constants obtained from  $\Phi_{A_{O_2}}$  measurements, are listed in Table 4.  $k_t$  was determined for all metal/edta complexes in H<sub>2</sub>O, and for edta in H<sub>2</sub>O and D<sub>2</sub>O. The rate constants of the Cu<sup>2+</sup> and the Fe<sup>3+</sup> complexes are average values of the results obtained from different metal/edta ratios.

The  $k_t$  values of edta and its metal complexes show that edta and its complexes with Al<sup>3+</sup> and Mn<sup>2+</sup> are poor <sup>1</sup>O<sub>2</sub> quenchers with  $k_t$  lower than 10<sup>6</sup> l·mol<sup>-1</sup>·s<sup>-1</sup>. The Al<sup>3+</sup> complex is in fact a less efficient quencher than edta (in D<sub>2</sub>O), and  $k_t$  of the Mn<sup>2+</sup> complex is identical to that of edta. The Cu<sup>2+</sup> and the Fe<sup>3+</sup> complexes are much more efficient <sup>1</sup>O<sub>2</sub> quenchers, with  $k_t$  higher than 10<sup>7</sup> l·mol<sup>-1</sup>·s<sup>-1</sup>, the latter showing a slightly higher value.

The rate constants  $k_r$  of the chemical reaction of <sup>1</sup>O<sub>2</sub> with edta in H<sub>2</sub>O increase in the order  $k_r(\text{Al}^{3+}/\text{edta}) < k_r(\text{edta}) \approx k_r(\text{Mn}^{2+}/\text{edta}) < k_r(\text{Cu}^{2+}/\text{edta}) < k_r(\text{Fe}^{3+}/\text{edta})$ . Al<sup>3+</sup> has no d electrons and exhibits diamagnetic character. Mn<sup>2+</sup> and Fe<sup>3+</sup> are isoelectronic d<sup>5</sup> ions, and Cu<sup>2+</sup> is a d<sup>9</sup> ion; these three ions have paramagnetic properties and form high-spin complexes with edta.

The rate constants  $k_q^{\text{H}_2\text{O}}$  of the physical quenching increase in the order:  $k_q(\text{edta}) \approx k_q(\text{Mn}^{2+}/\text{edta}) < k_q(\text{Al}^{3+}/\text{edta}) < k_q(\text{Cu}^{2+}/\text{edta}) < k_q(\text{Fe}^{3+}/\text{edta})$ . This sequence is similar to the one observed for the stability constants of these complexes [13].

$k_r$  Values are found to be consistently lower than  $k_q$  values (Table 5). The ratio  $k_q/k_r$  for edta is much higher in H<sub>2</sub>O than in D<sub>2</sub>O. The comparison between the values for edta in H<sub>2</sub>O and in D<sub>2</sub>O show a net increase of the ratio  $k_q/k_r$  in the protic solvent.  $k_q/k_r$  Ratios for the Al<sup>3+</sup>, Cu<sup>2+</sup>, and Fe<sup>3+</sup> complexes are much larger than that for free edta and reflect the sequence of  $k_q$  values shown above. For these three complexes, the  $k_r$  values are within the limits of error of  $k_q$  and are, therefore, negligible with respect to  $k_q$ .

Table 5. Ratio  $k_q/k_r$  (in H<sub>2</sub>O, unless otherwise indicated) and ratio  $k_t/k_r$  ( $k_r$  in H<sub>2</sub>O and  $k_t$  in D<sub>2</sub>O) for edta and Its Metal Complexes

	$\frac{k_q}{k_r}$	$\frac{k_r(\text{H}_2\text{O})}{k_r(\text{D}_2\text{O})}$		$\frac{k_q}{k_r}$	$\frac{k_t(\text{H}_2\text{O})}{k_t(\text{D}_2\text{O})}$
edta (D <sub>2</sub> O)	4.2(±0.5)		Al <sup>3+</sup> /edta	60(±12)	107(±58)
edta	8.7(±1.2)	6.9(±1.4)	Cu <sup>2+</sup> /edta	150(±100)	9.7(±5.6)
Mn <sup>2+</sup> /edta	6.7(±1.7)	9.1(±1.3)	Fe <sup>3+</sup> /edta	970(±250)	7.6(±1.7)

For singlet-oxygen quenching by amines, a mechanism involving electron-transfer or a partial-charge-transfer intermediate was suggested [17–21]. The results of the present work indicate that the complexed metal ion exercises an influence on a charge-transfer intermediate between the amine and <sup>1</sup>O<sub>2</sub>, the d electrons playing an important role. A spin inversion in the charge-transfer intermediate would result in physical quenching of <sup>1</sup>O<sub>2</sub> whereas chemical reaction of the complex may yield intermediates favoring the formation of oxidation products as proposed by Gollnick and Lindner [22]. In polar solvents, the charge-transfer intermediate would be expected to dissociate to form superoxide anion (O<sub>2</sub><sup>-</sup>) and the corresponding radical cation [23] [24]. As shown by  $k_q \gg k_r$ , the charged

oxygen species can apparently not dissociate and back transfer of the separated charges occurs. In addition to the amino group, carboxylic OH groups in edta may also act as  $^1\text{O}_2$  quenchers, as, at pH 9, one of the carboxylic acids remains protonated (pK 10.3 [25]). The quenching ability of OH groups shows a strong isotope effect [26].

The ratio of  $k_r/k_t$  (Table 5), where  $k_r$  and  $k_t$  represent the sum ( $k_r + k_q$ ) determined in  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$ , respectively, shows a surprisingly strong solvent effect for all complexes investigated. An increase of the quenching efficiency of approximately one order of magnitude is observed for free edta and for its metal complexes with  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Fe}^{3+}$ . This increase is even stronger for the  $\text{Al}^{3+}$  complex. Deuterium isotope effects have been reported for other  $^1\text{O}_2$  reactions; for instance, during the hydroperoxidation of olefins containing allylic H-atoms [27–29]. There,  $^1\text{O}_2$  reacts with the olefin to form an intermediate leading to the hydroperoxide by intramolecular H abstraction (ene reaction [7]). An intramolecular isotope effect  $k_H/k_D$  of ca. 1.4 was observed between competing H abstraction from CH and CD [27]. Studer *et al.* reported an increase of the rate constant of  $^1\text{O}_2$  quenching by flavone-3-ol by a factor of ca. 2.5 in  $\text{CH}_3\text{OH}$  compared to  $\text{CD}_3\text{OD}$  [30]. Tournaire *et al.* observed the same effect during the reaction of naphthalene-1,5-diol with  $^1\text{O}_2$  [31]. These authors observed reaction rate constants in  $\text{CH}_3\text{OH}$  which were by a factor of 1.4 to 1.5 higher than in  $\text{CD}_3\text{OD}$ . This isotope effect was explained by the deuteration of the OH groups by  $\text{CD}_3\text{OD}$  which slows down the proton transfer in the oxidation reaction. The isotope effect observed in this work for edta and its metal complexes is much stronger than those reported above. Both the rate constants of the physical quenching  $k_q$  and of the chemical reaction  $k_r$  are influenced. In the case of edta, the isotope effect for the reaction,  $k_r^{\text{H}_2\text{O}}/k_r^{\text{D}_2\text{O}}$ , is ca. 3.6 and for the physical quenching,  $k_q^{\text{H}_2\text{O}}/k_q^{\text{D}_2\text{O}}$ , ca. 7. An isotope exchange between the protonated COOH group of EDTA and the solvent is a plausible explanation for the isotope effect on  $k_q$ . Brauer and Schmidt [26] explain the different quenching capacities of OH and OD groups by an increase of the vibronic excitation energy changing from OH to OD. However, the effect of carboxylic OH or OD groups was not investigated in the literature. Therefore, a quantitative estimate of the isotope effect of the protonated COOH group of edta on the quenching of  $^1\text{O}_2$  is very difficult, in particular since it cannot be discriminated from the effect of the amino groups.

The isotope effect on the chemical reaction may be explained by the hypothesis that the carboxylic OH group is involved in the reaction. If we assume, as suggested by Gollnick and Lindner [22], that superoxide anion is formed during the reaction of  $^1\text{O}_2$  with amines, a nucleophilic attack from  $\text{O}_2^-$  on the carboxylic OH group is possible. A similar mechanism was suggested by Haugen and Whitten [32] for the photooxidation of aminoalcohols. For the metal/edta complexes, the isotope effect was determined only for the sum  $k_r$ , therefore, a mechanistic interpretation of potential effects on chemical reaction and physical quenching is not possible within the scope of this work.

Nevertheless, the very strong isotope effect in the case of the  $\text{Al}^{3+}$  complex, which is in fact the only complex exhibiting a lower rate constant  $k_r$  of the reaction and a higher rate constant  $k_q$  of the physical quenching than edta, confirms our working hypothesis that the isotope effect is more important on  $k_q$  than on  $k_r$ .

**4. Conclusions.** – The results reported in this paper show that the reactivity of edta and its metal complexes with  $^1\text{O}_2$  depend strongly on the complexed metal ion. Both, the



electronic configuration and the stability constants of the complex play a role on the kinetic parameters. The isotopic exchange between the complex and the solvent influences mainly the rate constant of physical quenching and, to a lesser extent, the rate constant of the chemical reaction.

**5. Experimental.** – *Chemicals.* Rose Bengal (*Fluka*) was used as a  $^1\text{O}_2$  sensitizer, edta as disodium salt (*Fluka*), and the metals in the chloride form ( $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ , *Fluka*;  $\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}$ , *Fluka*;  $\text{MnCl}_2 \cdot 4 \text{H}_2\text{O}$ , *Siegfried*;  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , *Merck*) were used without further purification. Buffer solns. (pH 9) were prepared with disodiumtetraborate ( $\text{Na}_2\text{B}_4\text{O}_7$ , *Merck*,  $16.2 \text{ g} \cdot \text{l}^{-1}$ ) and  $1.95 \text{ ml} \cdot \text{l}^{-1}$  HCl or DCl (38% in  $\text{D}_2\text{O}$  (*Fluka, puriss.*)).

*Methods. Luminescence Measurements.* The equipment used for the measurements of the  $^1\text{O}_2$  luminescence at 1270 nm upon continuous monochromatic excitation has already been described [5]. The *Stern-Volmer* measurements were done in  $\text{D}_2\text{O}$  at pH 9 with solns. of identical absorption ( $A = 1.8$ ) of the sensitizer at the wavelength of excitation ( $\lambda_{\text{ex}} = 547 \text{ nm}$ ). The solns. containing different concentrations of edta or of [metal]/(edta) complex were prepared from stock solns. of the sensitizer and of the substrate. The lifetime of  $^1\text{O}_2$  ( $\tau_d$ ) in  $\text{D}_2\text{O}$  pH 9 was measured on a time-resolved luminescence apparatus [33] and was found to be equal to  $60 (\pm 2) \mu\text{s}$ , in agreement with literature values [10] [11].

*Quantum-Yield Determinations.* The oxygen consumption ( $\Delta\text{O}_2\% < 10\%$ ) during irradiation was determined by following the decrease of the oxygen concentration by means of a Clark electrode. The electrode was inserted into a  $2 \times 2 \text{ cm}$  ( $V = 26 \text{ cm}^3$ ) closed cell. The solns. showed total absorption ( $A > 2$ ) at the irradiation wavelength ( $\lambda_{\text{ex}} = 546 \text{ nm}$ ). The samples were stirred, and the temp. was maintained at  $23^\circ$  at all times. The number of absorbed photons was determined from the voltage difference measured by a pair of bolometers and integrated during the irradiation time [15]. The bolometers were previously calibrated with *Aberchrome 540* as a chemical actinometer [7] [34].

The work of *D.P.H.* was financially supported by a research fund of *Deutscher Verein des Gas- und Wasserfachs (DVGW)*, Eichborn, Germany. Luminescence experiments were made at the *Ecole Polytechnique Fédérale de Lausanne (EPFL)*, Switzerland.

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