Photosensitized Autoxidation of Iron(II)

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Summary The rate of autoxidation of Fe^{II} in weakly acid solution is strongly increased by irradiation with visible light in the presence of eosin, presumably due to the participation of $^1\Delta_gO_2$.

VERY little quantitative work on photosensitized autoxidations in inorganic chemistry has been done.[1] We have investigated the photochemical oxidation of transition-metal ions by O_2 in the presence of potential photosensitizers with a view to obtaining evidence for the participation of singlet states of O_2 in the overall reaction.

We report here measurements of the rate of oxidation of iron(II) by molecular oxygen in aqueous perchlorate medium in the pH range 4·5—6·0 and in the presence of eosin. The overall reaction in weakly acid solutions is

$$4Fe^{2+}(aq) + O_2 \rightarrow 4FeO(OH)(aq) + 8H^+ \quad (1)$$

and the results are interpreted in terms of a mechanism involving the $^1\Delta_g$ state of O_2.

Reaction in absence of light. The reaction was followed (up to 2%), at a constant pH, by titrating the H^+ liberated according to eqn. (1)[2] using an automatic Radiometer pH-stat. The O_2 pressure was controlled by dilution with N_2 and measured by means of a Radiometer amperometric O_2-sensor in the gas stream.[3]

The dependence of the rate on pH is shown in Figure 1. These results together with results of measurements at various [Fe^{II}] are consistent with a rate law of the form (2) provided it can be assumed that [H^+] is less than about

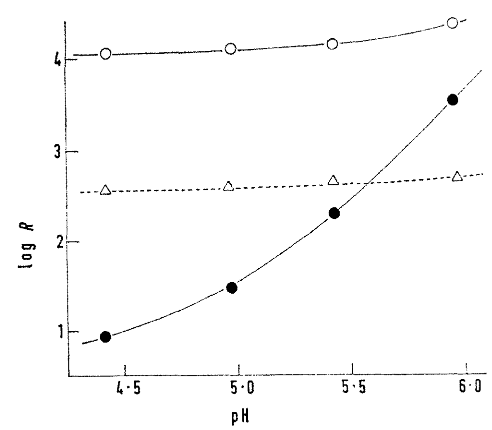

FIGURE 1. *Comparison of rate dependences on* pH. R *as* $-d[Fe^{II}]\,dt$ *in nmoles* $l.^{-1}min.^{-1}$ [Fe^{II}] = $1{\cdot}00 \times 10^{-3}$M, [*eosin*] = $1{\cdot}00 \times 10^{-5}$M. *White visible light was used.* T = $25{\cdot}00 \pm 0{\cdot}05°$. ●: *Dark reaction* ○: *Light reaction* (*corrected for dark reaction*), P_o = 1 *atm.* △: *Light reaction in purified* N_2.

$0{\cdot}1K$, where K is the first hydrolysis constant of Fe^{2+}.† P_{O_2} is the partial pressure of O_2.

$$-d[Fe^{II}]/dt = k_1[FeOH^+]{\cdot}P_{O_2} + k_2[FeOH^+]^2{\cdot}P_{O_2} + k_3{\cdot}[FeOH^+][Fe^{2+}]{\cdot}P_{O_2} \qquad (2)$$

The reaction paths corresponding to terms second-order in $[Fe^{II}]$ bear a close resemblance to the mechanisms suggested earlier[4,5] for the oxidation of Fe^{II} by O_2 in strongly acid solution. It is remarkable, however, that the collision complex between O_2 and $FeOH^+$ is stabilized enough by OH^- to make the bimolecular mechanism of comparable importance to the overall termolecular one.[6]

Eosin had no effect on the autoxidation rate of Fe^{II} in the dark, nor was its visible absorption spectrum influenced by the presence of Fe^{II} or O_2.

Reaction in presence of light. An optical cell of light path length 3·45 cm. was used as a reaction vessel, and it received a parallel light beam (3 cm. diameter) from a 6 v, 35 w tungsten lamp. A green filter transmitting in the range of the strong 516 nm. band of eosin was inserted in the light path, ensuring that all the transmitted light was absorbed in the cell containing the reaction solutions. The actual intensity was measured by chemical actinometry using the method of Wegner and Adamson.[7]

In the presence of eosin, a pronounced increase in rate, as compared to the dark reaction, is observed, and the reaction order in $[Fe^{II}]$ is now very close to 1. Figure 1 shows the influence of pH on the rate in 1 atm. O_2 and in 1 atm. N_2, purified from traces of O_2 by passage through a copper catalyst column. At higher $[H^+]$ a first-order dependence on $[OH^-]$ dominates, but the data do not fit a simple model over the entire pH range. Apparently, the rate of NaOH consumption in 1 atm. O_2 and in purified N_2 show approximately the same pH-dependence; we believe that this must be due to reaction between Fe^{II} and residual traces of O_2 (*ca.* 1 p.p.m.) in the N_2 atmosphere. The effect of varying P_{O_2} is shown in Figure 2, showing that the rate passes through a pronounced maximum as P_{O_2} increases.

No more than 1% of the eosin present was bleached during an experiment, equivalent to much less than the amount of Fe^{II} oxidized; also, at the light intensities used, no NaOH consumption could be detected when eosin solutions were irradiated in atmospheres of N_2 or O_2. This shows that only reactions of Fe^{II} are measured, and that eosin is not decomposed by radical reactions to any significant extent. Also, the quantum yields found (in moles of O_2 reacting per einstein absorbed) are considerably smaller than 1 (in the range of 0·01—0·08). We find that the energy-transfer mechanism originally suggested by Kautsky[8] provides the most natural explanation of the observed data. The main features are then[9] that by the irradiation, an excited state of eosin is formed, which transfers energy to the

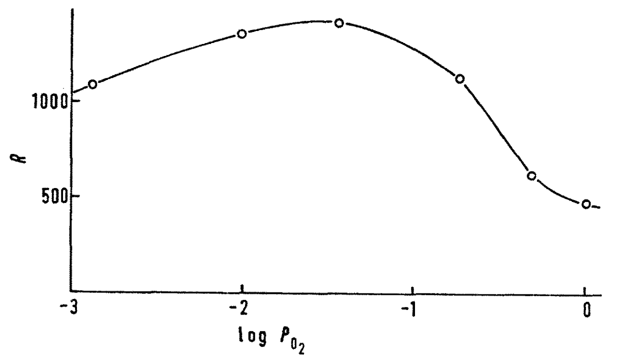

FIGURE 2. *Plot of rate against log* P_{O_2}. R *as* $-d[Fe^{II}]$ dt *in nmoles l.*$^{-1}$*min.*$^{-1}$, P_{O_2} *in atm.* $[Fe^{II}] = 1{\cdot}00 \times 10^{-3}$M, [*eosin*] $= 2{\cdot}00 \times 10^{-5}$M, pH $= 5{\cdot}00$, *and* $4{\cdot}3 \times 10^{-7}$ *einsteins/min. green light.* R *in purified* N_2 *is* 21×10^{-8}*moles l.*$^{-1}$*.min.*$^{-1}$.

${}^3\Sigma^-{}_g$ ground state of O_2, to form either ${}^1\Delta_g$ or ${}^1\Sigma^+{}_g$. Singlet O_2 is assumed to be the reactive intermediate in the photosensitized reaction. From the kinetic data alone, it is impossible to tell whether ${}^1\Delta_g$ or ${}^1\Sigma^+{}_g$ carries the burden of the oxidation of Fe^{II}, but as ${}^1\Sigma^+{}_g$ is known to be strongly quenched by H_2O (probably forming ${}^1\Delta_g$), we consider it to be ${}^1\Delta_gO_2$. The excited state of eosin involved is likely to be the lowest triplet, and the energy transfer reaction can then be written[9]

$$ {}^3S_1 + {}^3\Sigma_g^-O_2 \rightarrow {}^1S_0 + {}^1\Delta_gO_2 \qquad (3)$$

where S stands for eosin.

The decrease in the rate of the light-sensitized reaction with P_{O_2} for P_{O_2} greater than about $2{\cdot}10^{-2}$ atm. could be due to a spin-allowed quenching of the triplet dye, ${}^3S_2$, by the paramagnetic ground state O_2[10]

$$ {}^3S_1 + {}^3\Sigma_g^-O_2 \rightarrow {}^1S_0 + {}^3\Sigma_g^-O^2 \qquad (5)$$

This process would compete more strongly at higher P_{O_2}.

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† No reliable value of K for the medium used here is available.

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