

Catalytic Decomposition of Potassium Monopersulfate. The Kinetics

Olga Gimeno, Javier Rivas, Maria Carbajo, and Teresa Borralho

Abstract—Potassium monopersulfate has been decomposed in aqueous solution in the presence of Co(II). The process has been simulated by means of a mechanism based on elementary reactions. Rate constants have been taken from literature reports or, alternatively, assimilated to analogous reactions occurring in Fenton's chemistry. Several operating conditions have been successfully applied.

Keywords—Monopersulfate, Oxone®, Sulfate radicals, Water treatment.

I. INTRODUCTION

THE potassium monopersulfate molecule, (OXONE®), has recently attracted some attention in the removal of aqueous contaminants. OXONE® decomposition leads to the formation of free radicals [1]. The latter species are responsible of the oxidation of organic and inorganic pollutants. OXONE® scission can be carried out by homogenous catalysis in the presence of transition metals [2, 3]. The mechanism is similar to the well documented Fenton's chemistry. However, until now, there is a clear lack of proposals to explain the mechanism taking place when OXONE® is decomposed.

The number of potential reactions occurring in the homogeneous decomposition of OXONE® is too high to propose a complete reaction mechanism, however, from published data, a first approach to the actual set of reactions can be accomplished.

This study has been carried out with the aim of initiate a first advance in the kinetics of monopersulfate decomposition in the presence of cobaltous ion. Experimental data obtained under the influence of different operating variables have been used to obtain the unknown adjustable parameters.

II. MATERIALS AND PROCEDURE

OXONE® (Aldrich) decomposition was carried out in a jacketed cylindrical 2 L glass reactor equipped with sampling port, temperature controller, mechanic agitation and pH sensor. Temperature was regulated by circulating water through the reactor jacket. Initial pH of the reaction media

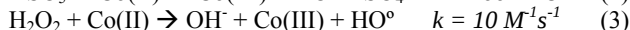
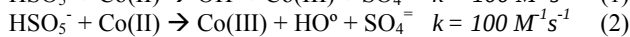
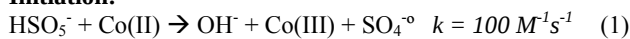
was achieved by addition of concentrated perchloric acid or sodium hydroxide depending on the predetermined conditions.

OXONE® was monitored with time by iodometric determination. Homogenous catalysis was Co(NO₃)₂ purchased from Panreac.

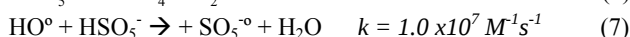
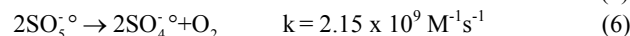
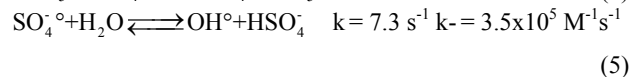
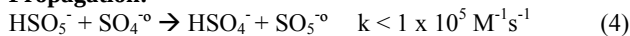
III. RESULTS AND DISCUSSION

As stated previously, the chemistry of the sulfate radical is not well established yet. Several reactions are under controversy or/and the true rate constants have not been documented. A survey on the past and recent literature regarding the different reactions involved in monopersulfate decomposition has allowed proposing the following reaction mechanism.

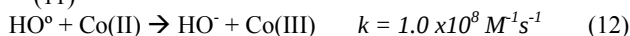
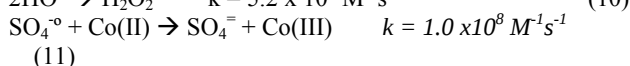
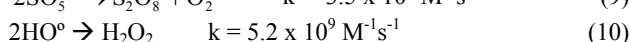
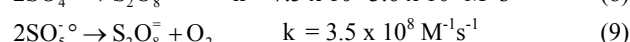
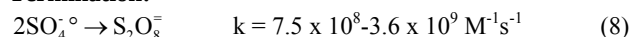
Initiation:



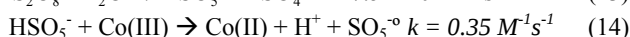
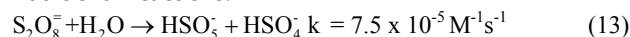
Propagation:



Termination:



Additional reactions:



The set of first order differential equations derived from reactions 1-14 was numerically solved by using the 4th order Runge Kutta approach.

Additionally, from the previous mechanism, the following considerations should be taken into account:

-Known rate constants have been taken from references [2, 4-7]. Unknown parameters are in italics.

-The initiation reactions 1-2 have been considered to have a value similar to the one reported for the catalysed

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decomposition of hydrogen peroxide by Fe(II) in pure water. Reaction 3 rate constant has been given a lower value. Cobalt (II) is not normally used in Fenton like reactions.

-Reaction 7 has been compared to the reaction of hydroxyl radicals with hydrogen peroxide. A similar value for the corresponding k value has been assumed.

-Reactions 11 and 12 have been considered to be similar to the reaction of $\text{HO}^\bullet$ radicals with Fe(II). Accordingly, an analogous rate constant has been chosen.

-Reaction 14 has been considered responsible of Co(II) regeneration. A regeneration stage has to be contemplated since in the absence of Co(II) the process would come to a halt. This rate constant was initially fitted by using one of the most representative runs. Thereafter the model was tested for the rest of operating conditions.

At this point, it has to be highlighted that the number of unknown parameters is too high, however, most of approximations have some logic behind and, likely, true rate constants should not be too different. To check for the validity of the proposed model, several operating conditions were tested.

i- Influence of Co(II) concentration

Traditionally, the kinetics of monopersulfate decomposition in the presence of Co(II) has been given order one regarding the catalyst concentration [8]. The proposed mechanism was applied in a interval of Co(II) concentration from 1.0×10^{-5} to 20×10^{-4} M.

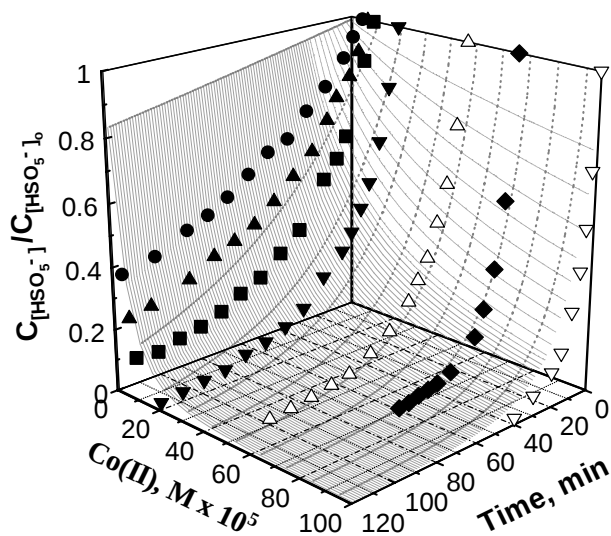


Fig. 1 Homogeneous catalytic decomposition of HSO_5^- by Co(II). Experimental conditions: $T = 20^\circ\text{C}$, initial $\text{pH} = 2.0$, $V = 2\text{ L}$, $C_{\text{HSO}_5^-} = 0.01\text{ M}$, $C_{\text{Co(II)}} = (M \times 10^4)$: $\blacklozenge$, 6.9; ∇ , 10.0; $\blacktriangledown$, 2.1; $\blacksquare$, 1.0; $\bullet$, 0.5; $\blacktriangle$, 0.75; $\triangle$, 5.0. (Mesh: model simulation)

As observed from Fig. 1, the model acceptably simulates the monopersulfate depletion profiles in the presence of varying amounts of cobalt. From theoretical data the order kinetics regarding catalyst concentration could be calculated

(first order regarding monopersulfate concentration was assumed).

Thus, the following figure shows the natural logarithm of the apparent pseudofirst order rate constant versus the corresponding logarithm for cobalt concentration.

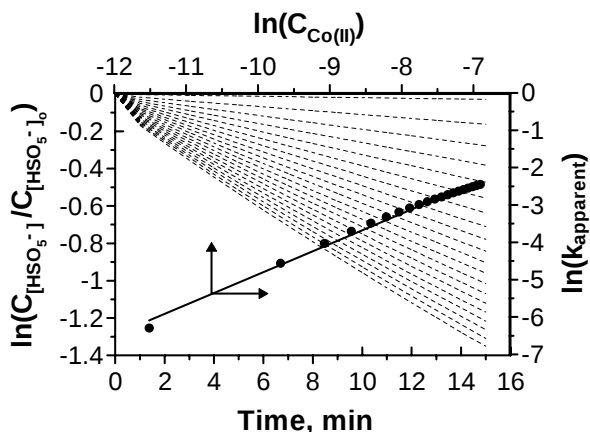


Fig. 2 Homogeneous catalytic decomposition of HSO_5^- by Co(II). Experimental conditions as in Fig. 1. Theoretical reaction order regarding catalyst concentration

From Fig. 2 a theoretical reaction order for cobalt of roughly 0.82 was obtained, similar to the experimental value of 0.8 and close to 1.0 given by other authors [8].

ii- Influence of monopersulfate concentration

The reaction order regarding monopersulfate concentration has been reported to be one [8].

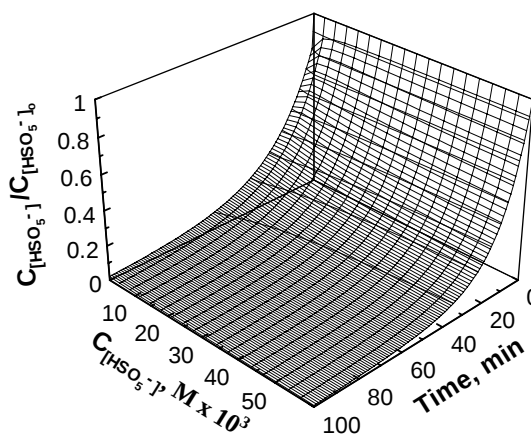


Fig. 3 Homogeneous catalytic decomposition of HSO_5^- by Co(II). Experimental conditions: $T = 20^\circ\text{C}$, initial $\text{pH} = 2.0$, $V = 2\text{ L}$, $C_{\text{Co(II)}} = 5 \times 10^{-4}$. Model simulation

Experiments carried out at different initial concentration of monopersulfate led to negative values of the reaction order. However, the latter results were the consequence of using a different initial pH (it has to be pointed out the acidic nature of OXONE®). A more exhaustive analysis of monopersulfate influence resulted in a concordance with literature data. The

proposed model avoided pH problems (it was assumed to be constant in the set of differential equations) and could simulate the OXONE® profiles with time by keeping constant the rest of operating variables. Fig. 3 shows the results obtained at pH 2.

As illustrated in Fig. 3, OXONE® initial concentration does not significantly affect its conversion profile, typical of first order systems.

iii- Influence of pH

pH is one of the most important parameters in Fenton's chemistry. Analogously, this parameter is fundamental in monopersulfate decomposition in the presence of cobalt (II). It is postulated that pH must influence to a higher extent reactions between molecules rather than reactions involving radicals. Thus, initiation reactions (1-3) and cobalt regeneration (reaction 14) are suggested to be clearly influenced by pH. Likely, some of them involve the formation of complexes governed by pH media. A sensitivity analysis of the aforementioned rate constants revealed that the controlling stage was cobalt regeneration. As a consequence, it was decided to adjust k_{14} to minimize differences between experimental and calculated results. The dependence of k_{14} with pH was thereafter assessed.

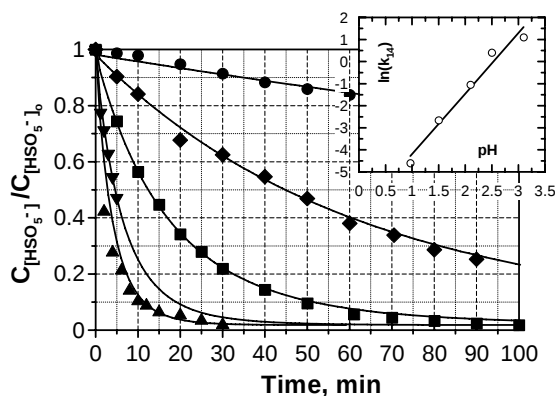


Fig. 4 Homogeneous catalytic decomposition of HSO_5^- by Co(II) . Experimental conditions: $T = 20^\circ\text{C}$, $V = 2\text{ L}$, $C_{\text{Co(II)}} = 5.0 \times 10^{-4}\text{ M}$, $C_{\text{HSO}_5^-} = 0.01\text{ M}$, $\text{pH} = (\text{initial})$: $\bullet$, 0.97; $\blacklozenge$, 1.5; $\blacksquare$, 2.1; $\blacktriangledown$, 2.5; $\blacktriangle$, 3.1. (lines: model calculations)

Fig. 4 shows the fitted monopersulfate profiles and the excellent concordance with experimental results. Also, the inset in this figure shows the relationship between pH and k_{14} . The expression relating both parameters is:

$$\ln(k_{14}) = -6.94 + 2.74 \text{ pH} \quad R^2 = 0.97 \quad (15)$$

iv-Influence of temperature

Temperature effect was investigated in the interval $8.5 - 30^\circ\text{C}$. Similarly to pH influence, it was suggested that this parameter predominantly influenced k_{14} . Consequently, this parameter was again fitted to minimize experimental and model monopersulfate depletion profiles.

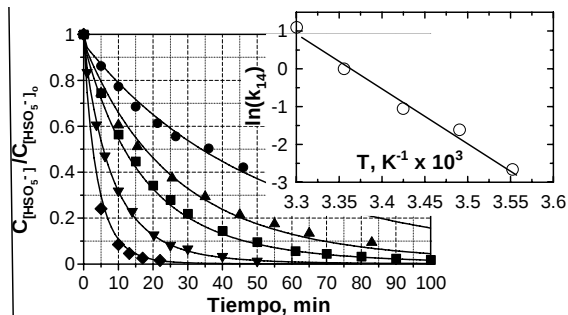


Fig. 5 Homogeneous catalytic decomposition of HSO_5^- by Co(II) . Experimental conditions: $V = 2\text{ L}$, $C_{\text{Co(II)}} = 5.0 \times 10^{-4}\text{ M}$, $C_{\text{HSO}_5^-} = 0.01\text{ M}$, $\text{pH} = 2.1$, $T = (^\circ\text{C})$: $\bullet$, 8.5; $\blacktriangle$, 13.5; $\blacksquare$, 19; $\blacktriangledown$, 25; $\blacklozenge$, 30. (Lines: model calculations)

Fig. 5 illustrates the notorious influence of temperature on the monopersulfate depletion profiles. The proposed model acceptably simulates the OXONE® conversion by just considering the Arrhenius dependence of k_{14} on temperature (in Kelvin) at pH 2.1 (see inset in Fig. 5):

$$\ln(k_{14}) = 48.5 - 14400/T \quad R^2 = 0.98 \quad (16)$$

Fig. 6 depicts the influence of temperature by considering a wider range of temperatures.

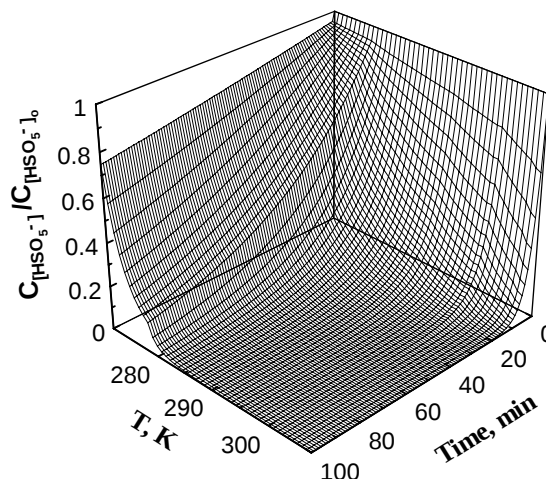


Fig. 6 Homogeneous catalytic decomposition of HSO_5^- by Co(II) . Experimental conditions: $V = 2\text{ L}$, $C_{\text{Co(II)}} = 5.0 \times 10^{-4}\text{ M}$, $C_{\text{HSO}_5^-} = 0.01\text{ M}$, $\text{pH} = 2.1$. Model simulation

From the previous discussion it is suggested that reaction 14, i.e. cobalt regeneration, is fundamental in this system.

Two more experiments were carried out in the presence of free radical scavengers to avoid monopersulfate decomposition through reactions 4 and 7.

Fig. 7 shows the results obtained in the presence of 0.01 M of methanol or tert-butyl alcohol.

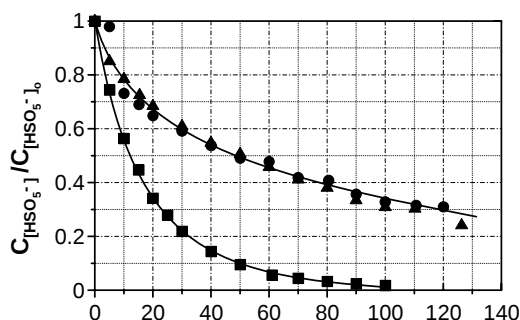


Fig. 7 Homogeneous catalytic decomposition of HSO_5^- by Co(II) . Experimental conditions: $V = 2 \text{ L}$, $C_{\text{Co(II)}} = 5.0 \times 10^{-4} \text{ M}$, $C_{\text{HSO}_5^-} = 0.01 \text{ M}$, $\text{pH} = 2.1$, $T = 20^\circ \text{C}$. ●, 0.01 M methanol; ▲, 0.01 M tert-butanol; ■, No scavenger

Fig. 7 demonstrates that radicals play an important role in monopersulfate decomposition. By assuming that radicals have been trapped by the scavengers, a simple pseudofirst order kinetics can be applied so the rate constant of monopersulfate with cobalt can be tentatively determined. The results should be taken with caution because scavengers can also interfere in the formation of complexes needed for monopersulfate decomposition.

Fig. 8 shows the aforementioned pseudofirst order plot.

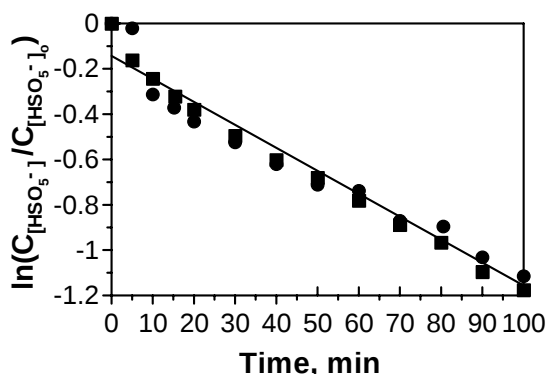


Fig. 8 Homogeneous catalytic decomposition of HSO_5^- by Co(II) . Experimental conditions: $V = 2 \text{ L}$, $C_{\text{Co(II)}} = 5.0 \times 10^{-4} \text{ M}$, $C_{\text{HSO}_5^-} = 0.01 \text{ M}$, $\text{pH} = 2.1$, $T = 20^\circ \text{C}$. ●, 0.01 M methanol; ■, 0.01 M tert-butanol

From the slope in Fig. 8, the calculated pseudofirst order rate constant was $1.67 \times 10^{-4} \text{ s}^{-1}$, i.e. after dividing by cobalt concentration, the second order rate constant is $0.34 \text{ M}^{-1} \text{ s}^{-1}$, similar to $0.35 \text{ M}^{-1} \text{ s}^{-1}$ obtained after fitting k_{14} in the proposed model. It is hypothesized that reaction 14 does control the process in the absence of radicals and is a key stage in monopersulfate decomposition.

IV. CONCLUSION

-An attempt has been made to simulate the monopersulfate decomposition in the presence of Co(II) . For this purpose, a set of elementary reactions have been considered. Some of them have been taken from the literature while others have

been related to the analogous Fenton's chemistry.

-The mechanism is capable of acceptably simulate monopersulfate decomposition under different conditions of temperature, pH and reagents concentration.

-A Co(II) regeneration stage is envisaged as a crucial step in the process.

-A number of rate constants have been assumed. Future work on determining these unknown parameters is advised.

-Other reactions not considered in this study should also be contemplated in some particular systems (i.e. inefficient monopersulfate decomposition, formation of complexes, etc.)

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