Catalytic Decomposition of Potassium Monopersulfate. Influence of Variables

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

Abstract—Potassium monopersulfate has been decomposed in aqueous solution in the presence of Co(II). The effect of the main operating variables has been assessed. Minimum variations in pH exert a considerable influence on the process kinetics. Thus, when no pH adjustment is considered, the actual effect of variables like initial monopersulfate and/or catalyst concentration may be hindered. As expected, temperature enhances the monopersulfate decomposition rate by following the Arrhenius law. The activation energy in the proximity of 85 kJ/mol has been obtained. Amongst the different solids tested in the monopersulfate decomposition, only the perovskite $LaTi_{0.15}Cu_{0.85}O_3$ has shown a significant catalytic activity.

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

I. INTRODUCTION

THE potassium monopersulfate molecule, commercially known as OXONE®, has recently attracted some attention in the removal of contaminants dissolved in water. The increasing application of OXONE® in water remediation studies relies on the potential oxidizing capacity of the radicals generated after its decomposition [1]. The monopersulfate molecule scission can be carried out by homogenous catalysis in the presence of transition metals [2], heterogeneous catalysis by oxides [3], from the application of radiant energy [4] or by simple thermal decomposition [1].

From a practical point of view, application of OXONE® has been limited to chlorine complement in swimming pools disinfection. At laboratory scale some authors have investigated the potential of OXONE® in the removal of phenols, HAPs, pesticides, and dyes [5] - [7].

Although OXONE® is raising some expectation as an alternative water remediation technology; the number of works focused on its decomposition kinetics is rather low. Accordingly, this study has been carried out with the aim of elucidating the influence of some operating variables in OXONE® decomposition when either Co(II) is used as homogenous catalyst or a perovskite solid is utilized as heterogeneous catalyst. Use of heterogeneous catalysis is highly recommended due to advantages like easiness of catalyst separation, wider range of working pH, etc.

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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 were $Co(NO_3)_2$, $FeSO_4$, $CuSO_4$, $MnSO_4$, $Ti_2(SO4)_3$. All of them were purchased from Panreac. Heterogeneous catalytic experiments were conducted by using a perovskite type catalyst synthesized in the laboratory [8]. The solid catalyst was tested in slurry mode by addition of the solid directly into the aqueous OXONE® solution.
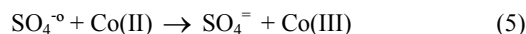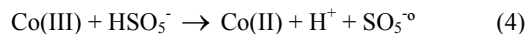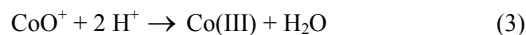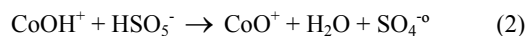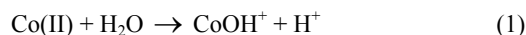
III. RESULTS AND DISCUSSION

A. Homogeneous Catalysis

Several transition metals Co(II), Fe(II), Cu(II), Mn(II), and Ti(III) were tested to assess their potential catalytic activity in the monopersulfate decomposition reaction. However, only Co(II) showed an appreciable activity. Accordingly, this metal was thereafter used in this study.

i- Influence of Co(II) concentration

The catalytic mechanism involving Co(II) suggests that this metal participates in a redox cycle preventing the precipitation of the insoluble $Co(OH)_3$ ($K_S = 3.2 \times 10^{-45}$).

$$Co(II) + H_2O \rightarrow CoOH^+ + H^+ \qquad (1)$$

$$CoOH^+ + HSO_5^- \rightarrow CoO^+ + H_2O + SO_4^{-o} \qquad (2)$$

$$CoO^+ + 2 H^+ \rightarrow Co(III) + H_2O \qquad (3)$$

$$Co(III) + HSO_5^- \rightarrow Co(II) + H^+ + SO_5^{-o} \qquad (4)$$

$$SO_4^{-o} + Co(II) \rightarrow SO_4^= + Co(III) \qquad (5)$$

Traditionally, the catalyst kinetic order for OXONE® decomposition has been assumed unity in a wide range of pH [9]. Fig. 1 shows the evolution profiles for the normalized monopersulfate concentration with time for a series of experiments conducted under different initial Co(II) amounts.
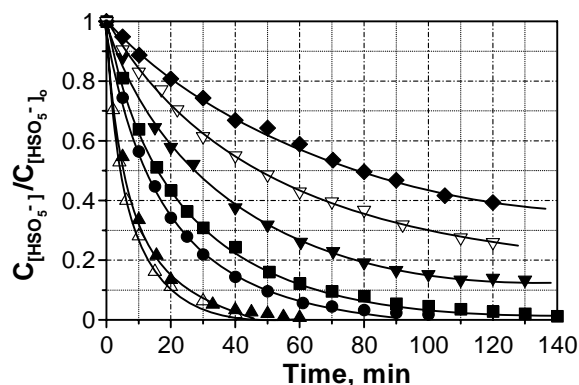
Fig. 1 Homogeneous catalytic decomposition of HSO_5^- by Co(II). Experimental conditions: T = 20 °C, initial pH = 2.0, V = 2 L, C_{HSO5^-o} = 0.01 M, $C_{Co(II)}$ = (M x 10^4): ♦, 0.50; ▽, 0.75; ▼, 1.0; ■, 2.1; ●, 5.0; ▲, 6.9; △, 10.0.

At the sight of HSO_5^- concentration curvature in Fig. 1, it is suggested that this species follows simple first order kinetics so a plot of the natural logarithm of monopersulfate concentration versus time should yield a straight line (see (6)).

$$\ln\left[\frac{C_{HSO_{5o}^-}}{C_{HSO_5^-}}\right]_{t=0} = k\frac{C_{Co(II)}^n}{C_{H^+}^m} \times t = k_{Observed} \times t \qquad (6)$$

Additionally, if initial rates are only considered it follows that:

$$\ln[-r_o] = \ln\left[-\frac{dC_{HSO_5^-}}{dt}\right]_{t=0} = n \times \ln\left[C_{Co(II)}\right]_{t=0} + Const. \qquad (7)$$

From (6) and (7) the value of "n" could be deduced through the convenient plot (see Fig. 2).
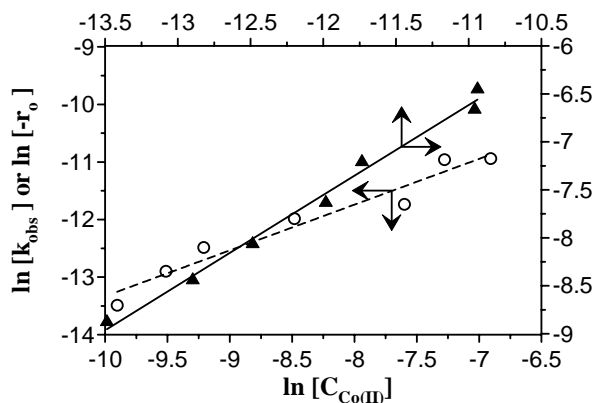

Fig. 2 Homogeneous catalytic decomposition of HSO_5^- by Co(II). Experimental conditions as in Fig. 1. O, $\ln(-r_o)$; ▲, $\ln(k_{Observed})$

Slope values of 0.8 and 0.93 were obtained for plots of $\ln(-r_o)$; and $\ln(k_{Observed})$, respectively, close to the first order reported in the literature. Differences could be attributed to small changes in pH, both at the beginning of the process and along the reaction.

ii- Influence of HSO_5^- concentration.

According to previous studies [9], the apparent reaction order of monopersulfate decomposition in the presence of Co(II) is one. This statement was analyzed by conducting an experimental reaction series by varying the initial OXONE® concentration. Fig. 3 shows the results obtained:
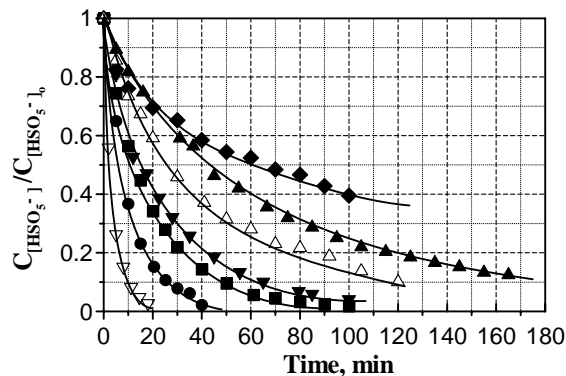

Fig. 3 Homogeneous catalytic decomposition of HSO_5^- by Co(II). Experimental conditions: T = 20 °C, initial pH range= 1.73-2.56, V = 2 L, $C_{Co(II)}$ = 5 x 10^{-4} M, $C_{HSO_5^-o}$ = (M x 10^3): ♦, 60; ▲, 37; △, 28; ▼, 19; ■, 8.5; ●, 4.5; ▽, 1.9.

From Fig. 3 it is initially deduced that HSO_5^- decomposition does not follow a first order kinetics. However in these experiments an important parameter has not been considered. Thus, potassium monopersulfate is a weak acid (pK = 9.2) and different initial concentrations of this acid lead to different initial reaction pH´s. In other circumstances, the aforementioned differences are rather negligible and should not appreciably influence the kinetics of the process, however, proton concentration is a key parameter in HSO_5^- decomposition and these small differences in pH are enough to significantly vary the reaction rate. Therefore, the method of initial rates was adopted by considering the initial pH in each case and order -1 regarding protons concentration. If reported kinetics are right, a plot of $\ln(-r_o)$ versus

$$\ln\left[\frac{C_{HSO_5^-}}{C_{H^+}}\right]_{t=0}$$ should lead to a straight line of slope unity.

Fig. 4 shows the aforementioned plot. The slope of the straight line was 0.90 (R^2 = 0.92), close to the experimental value given in other works.

Given the significant role played by H^+, a final series was completed by adjusting the initial pH of the reaction in the interval 0.97 – 3.1.
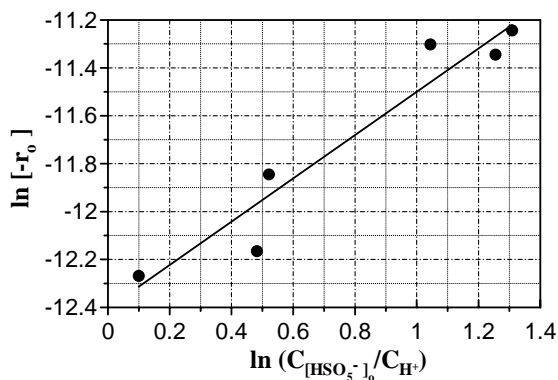
Fig. 4 Homogeneous catalytic decomposition of HSO_5^- by Co(II). Experimental conditions as in Fig. 3

iii-Influence of initial pH

The influence of protons is limited by the low solubility of cobalt hydroxides. Thus, the range of pH was investigated between 1.0 and 3.1. Fig. 5 shows the results obtained.
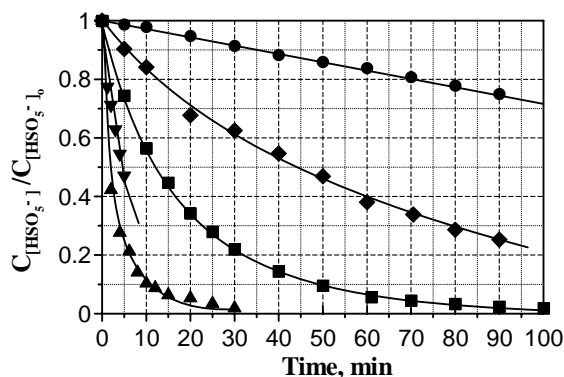

Fig. 5 Homogeneous catalytic decomposition of HSO_5^- by Co(II). Experimental conditions: T = 20 ºC, V = 2 L, $C_{Co(II)}$ = 5.0 x 10^{-4} M, C_{HSO5^-o} = 0.01 M, pH = (initial): ●, 0.97; ♦, 1.5; ■, 2.1; ▼, 2.5; ▲, 3.1

As observed, the higher the initial pH, the higher the conversion rate for monopersulfate depletion. Although pH was not strictly constant along the whole reaction period, the observed rate constant calculated from the profiles in Fig. 4 were used to determine the H^+ reaction order. Additionally, data at time zero were also used (no pH change) to calculate the same parameter. The slope calculated in the plots ln(-r_o); or ln($k_{Observed}$) versus ln(C_{H+}) led to values of -1.02 in both cases.

iv-Influence of temperature

Temperature effect was investigated in the interval 8.5 – 30 ºC. Fig. 6 illustrates the normalized evolution profiles of the monopersulfate concentration as a function of time.
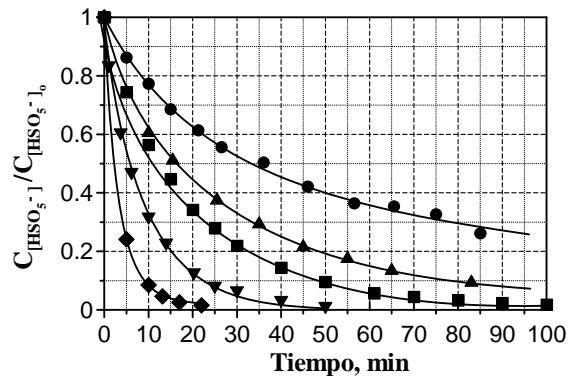

Fig. 6 Homogeneous catalytic decomposition of HSO_5^- by Co(II). Experimental conditions: V = 2 L, $C_{Co(II)}$ = 5.0 x 10^{-4} M, C_{HSO5^-o} = 0.01 M, pH = 2.1, T = (ºC): ●, 8.5; ▲, 13.5; ■, 19; ▼, 25; ♦, 30

As expected, temperature exerted a positive influence on monopersulfate decomposition, however, this faster decomposition does not involve a higher generation of free radicals. Similarly to hydrogen peroxide decomposition, an excessive temperature might induce a higher fraction of inefficient decomposition into sulfate and oxygen.

An Arrhenius plot of the observed rate constants led to an activation energy of 85 kJ/mol. However if initial rates are considered, this value dropped to 60 kJ/mol although a lower correlation coefficient was obtained (see Fig. 7). The first value seems to be more accurate.
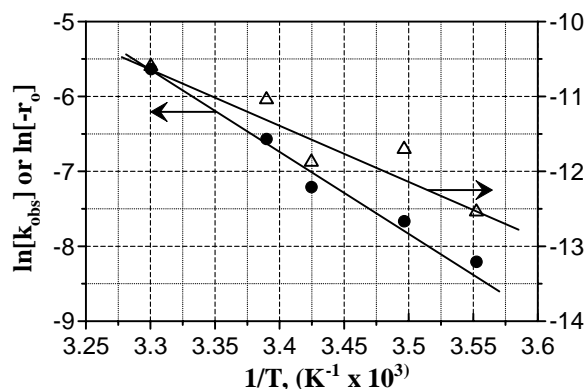

Fig. 7 Arrhenius plot for the homogeneous catalytic decomposition of HSO_5^- by Co(II). Experimental conditions as in Fig. 6. Δ, ln(-r_o); ●, ln($k_{Observed}$)

B. Heterogeneous Catalysis

i-Influence of catalyst load

Several solids were tested to assess their catalytic activity in monopersulfate decomposition. Goethite, ruthenium supported on ceria, and platinum supported on alumina did show no significant catalytic activity. Only the perovskite $LaTi_{0.15}Cu_{0.85}O_3$ offered a considerable effect on OXONE® disappearance. This solid has also been used in catalytic ozonation processes [8]. Fig. 8 displays the influence of this catalyst at pH 7.0.
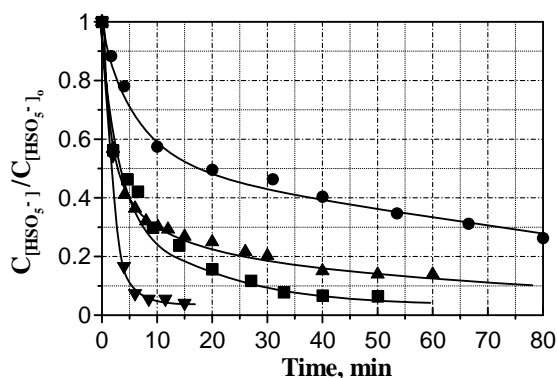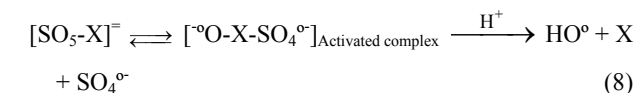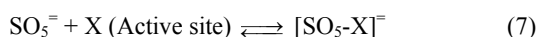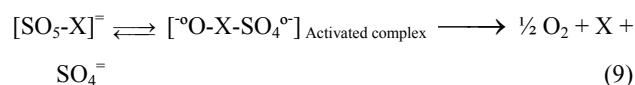
Fig. 8 Heterogeneous catalytic decomposition of HSO_5^- by $LaTi_{0.15}Cu_{0.85}O_3$. Experimental conditions: T = 20 ºC, V = 2 L, $C_{HSO_5^-o}$ = 0.01 M, pH = 7.0 (initial); Solid concentration (g/L): ●, 0.1; ▲, 0.25; ■,0.50; ▼, 1.00.

Fig. 9 Heterogeneous catalytic decomposition of HSO_5^- by $LaTi_{0.15}Cu_{0.85}O_3$. Experimental conditions: T = 20 ºC, V = 2 L, $C_{HSO_5^-o}$ = 0.01 M, Solid concentration 0.5 g/L; pH = (initial): ●, 4.5; ▲, 5.3; ■,6.6; ▼, 11.3.

The mechanism of monopersulfate decomposition must involve an adsorption stage onto active sites similar to the one described by (6) – (9).

$$HSO_5^- \rightleftharpoons SO_5^= + H^+ \qquad (6)$$

$$SO_5^= + X \text{ (Active site)} \rightleftharpoons [SO_5\text{-}X]^= \qquad (7)$$

$$[SO_5\text{-}X]^= \rightleftharpoons [^\circ O\text{-}X\text{-}SO_4^{\circ-}]_{\text{Activated complex}} \xrightarrow{H^+} HO^\circ + X$$
$$+ SO_4^{\circ-} \qquad (8)$$

or alternatively:

$$[SO_5\text{-}X]^= \rightleftharpoons [^\circ O\text{-}X\text{-}SO_4^{\circ-}]_{\text{Activated complex}} \longrightarrow \tfrac{1}{2} O_2 + X +$$
$$SO_4^= \qquad (9)$$

Obviously, from an environmental point of view (8) is the preferred pathway in terms of oxidising agent generation. The predominance of (8) or (9) is out of the scope of this study and will be addressed in the future.

ii- Influence of HSO_5^- concentration.

Contrarily to homogeneous experiments, monopersulfate initial concentration did not affect its evolution conversion with time (results not shown). It is suggested that under the operating conditions used in this study, first order kinetics apply to the peroxide concentration.

iii- Influence of reaction pH.

As observed in Fig. 9 pH exerts a crucial role in monopersulfate decomposition, likely the adsorption process is favored at high pH when the dissociation percentage of the molecule is increased. An increase in pH is also beneficial in terms of metal leaching. Thus, release of active metallic species from solid catalysts is normally associated to low pH values.
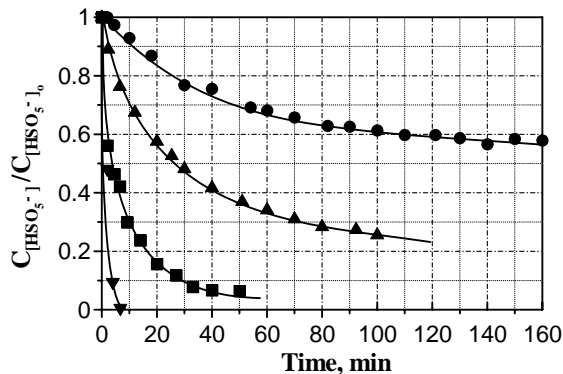
IV. CONCLUSION

Sulfate radicals generated after the decomposition of OXONE® seems to be a promising alternative in wastewater treatment. The potential application of these radicals is similar to the well known hydroxyl radicals, however some controversial aspects should be addressed before scaling up of this technology:

-The $SO_4^=$ formed as an end product has to be considered. Removal of sulfates should comply with regulatory limits.

-Similarly to sulfates, if homogenous catalysts are used (e.g. Co(II)), these have to be removed and reused from the treated effluent.

-Development of heterogeneous catalyst should be encouraged when contemplating this technology. Moreover, Supporting of heterogeneous catalyst should also be preferred to slurry modes of action.

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