CATALYTIC AGENT DEGRADATION ON OXIDE FILMS AND IN MICHEMETERGEOUS SOLUTION SYSTEMS

First Interim Report
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Experimental efforts related to Contract no. DAJA45-90-C-0007 entitled "Catalytic Agent Degradation on Oxide Films and in Microneterogeneous Solution Systems" is described in this first technical report (December 8, 1989 -- February 8, 1990). Emphasis in the first two months of research has been placed on thermal degradations in aqueous dispersions of colloidal semiconductors (precisely, TiO$_2$) and on TiO$_2$ films containing CW simulants and strong oxidants. Catalytic agents were employed to enhance these decompositions. The experiments with dispersions are extensions of preliminary studies in this area. Thin film systems have likewise been examined.

As mentioned earlier thermal decompositions of organophosphorous compounds were not witnessed in the presence of powerful oxidants such as hydrogen peroxide, periodate and bromate alone. Only K$_2$S$_2$O$_8$ had a high enough reactivity to allow thermal activated decomposition and enough oxidizing power to push forward these degradations without the adjunction of catalytic agents, e.g. AgNO$_3$, although only at sufficiently elevated temperatures. (In presence of an adequate concentration of AgNO$_3$ the reaction could proceed at ambient temperature.)

Previous experiments likewise demonstrated the feasibility of using alternative redox catalysts such as Fe$_2$SO$_4$, Co(NO$_3$)$_2$, and Ni(NO$_3$)$_2$, with only Fe$_2$SO$_4$ yielding promising results. The relative success with Fe$_2$SO$_4$ lead our experimental endeavors in testing Fe$_2$(SO$_4$)$_3$ as a possible catalytic agent.

Fe (III) ions catalyze efficiently the total oxidation of simulants by H$_2$O$_2$

The usage of Fe$_2$(SO$_4$)$_3$ as a catalyst in these degradation reactions proved to be an important discovery. Fe$_2$(SO$_4$)$_3$ is a cheap and readily available compound which has no harmful effect on the environment. It was found to greatly accelerate the total oxidation of phosphate ester simulants in aqueous environment even at relatively low concentrations.

The catalytic effect of Fe$_2$(SO$_4$)$_3$ is demonstrated in Fig. 1 where the decomposition of 4-NPIPP (4-nitrophenylisopropylphenyl phosphinate) evaluated by CO$_2$ evolution as a function of catalyst concentration is depicted.

All aqueous dispersions were prepared by the following technique. The appropriate quantity of 10$^{-1}$ M simulant solution (THF solvent) was injected onto the reaction vessels' walls and the solvent evaporated by heating until no traces of solvent were left. Subsequently, the simulant was redissolved in water. In Fig. 1, titanium dioxide (P25, Degussa, 5g/l) was also present. (The role of
TiO$_2$ in the degradation process of the simulant is further elucidated below.

The total oxidation of 4-NPIPP obeys the stoichiometry:

$$\text{NO}_2 \text{P} \quad + \quad 19.5 \text{O}_2 \quad \rightarrow \quad 15 \text{CO}_2 \quad + \quad \text{H}_3\text{PO}_4$$

$$+ \quad \text{HNO}_3 \quad + \quad 6 \text{H}_2\text{O}$$

This reaction was followed by analysis of the CO$_2$ evolved. High pressure liquid chromatography (HPLC) data confirmed quantitatively these decomposition reactions through reactant loss.

Figure 1 shows that the degradation of 4-NPIPP at 50°C goes progressively faster and nearer to completion as the concentration of Fe$_2$(SO$_4$)$_3$ increases (only a small difference in reaction rate and yield is noted between the two upper concentration limits of 5.10$^{-3}$ M and 1.10$^{-2}$ M). At these Fe(III) concentrations the mineralisation of the simulant is achieved within minutes while in the absence of Fe (III) only a small fraction of the agent was degraded after 2.5 hours.

In order to rationalize this dramatic catalytic effect we evoke tentatively the participation of iron species having a higher oxidation state than III. Since Fe(II) displays significantly lower catalytic activity in the decomposition of phosphate esters than Fe(III) a simple Haber-Weiss type mechanism alone cannot explain the present observations. At pH's greater than 2 (this experimental work is generally carried out at pH's between 5 and 6) iron (III) is highly hydrolyzed and forms oligomeric structures:

$$\text{HO} \quad - \quad \text{Fe}^{3+} \cdot \text{O} \cdot \text{Fe}^{3+} \cdot \text{O} \cdot \text{Fe}^{3+} \cdot -$$

The rapid oxidation of the organophosphate compounds takes place by reaction with an Fe (IV) complex, an extremely powerful oxidant, formed by O-transfer from hydrogen peroxide, according to the following reaction:

$$\text{OH} \quad \left[ - \text{Fe} \cdot \text{O} \cdot \right]_n \quad + \quad \text{H}_2\text{O}_2 \quad \rightarrow \quad \text{H}_2\text{O} \quad + \quad \text{OH}^- \quad + \quad \left[ - \text{Fe}^{(IV)+} \cdot \text{O} \cdot - \right]_n$$

(2)
As the organophosphate is subsequently oxidized Fe(IV) is regenerated into Fe(III) thus maintaining its catalytic status. Hydrogen peroxide is exhausted as a sacrificial oxidant.

At higher temperatures aqueous solutions of H₂O₂ may be rapidly decomposed into water and oxygen decreasing the prominence of this Fe (IV) reaction pathway and allowing the decomposition to occur via other pathways. Concentrations of Fe₂(SO₄)₃ and H₂O₂ and the reaction temperature have to be adjusted in order to optimize the Fe (IV) reaction pathway. The eventuality of a Haber-Weiss type reaction such as is believed to happen in presence of FeSO₄ (specifically a Fenton reaction):

\[
\text{H}_2\text{O}_2 + e^- \rightarrow \text{OH}^- + \cdot\text{OH} \quad \text{(Haber-Weiss)} \quad (3)
\]

\[
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{OH}^- + \cdot\text{OH} + \text{Fe}^{3+} \quad \text{(Fenton reaction)} \quad (4)
\]

with subsequent oxidation of the CW simulant by hydroxyl radicals cannot be discounted if Fe³⁺ is initially reduced by the organic moieties of the organophosphorous compounds. There is not enough energy available at the temperatures studied to allow the formation of hydroxyl radicals by simple thermal dissociation (~1 eV binding energy for H₂O₂), as is possible at elevated temperatures for persulfate.

Titanium dioxide sustains the oxidizing action of hydrogen peroxide by formation of surface peroxides

TiO₂ plays a stabilizing role in these experiments. This effect is shown in Figs. II and III at 70°C and at constant concentration of Fe₂(SO₄)₃ (i.e. 10⁻³ M) where the decomposition of 4-NPP (CO₂ evolution) at various concentrations of H₂O₂ is illustrated. Without TiO₂ present (Fig. II) the lower concentrations of H₂O₂ are much less effective in the decomposition of 4-NPP than when TiO₂ is present at 5 gm/l (Fig. III). In TiO₂ containing solutions there is very little difference in degradation efficiency between 0.02 M and 1 M H₂O₂. The surface of TiO₂ must therefore play a decisive role in sustaining the oxidative action of H₂O₂. In TiO₂-free solution the H₂O₂ decomposes by disproportionation into oxygen and water. This competes with the H₂O₂ reaction with agent explaining the incomplete nature of simulant degradation at the lower H₂O₂ concentration. In the presence of TiO₂ the H₂O₂ is bound to the surface forming titanium
peroxo complexes which do not undergo such disproportionation. The important role of TiO$_2$ which emerges from these studies is that it stabilizes the peroxide while maintaining its high oxidation power.

Preliminary experiments with thin films of TiO$_2$

The degradation of 4-NPDEP (paraoxon, 4-nitrophenyldiethylphosphate) on TiO$_2$ fractal electrodes was examined in presence of various catalytic agents. These electrodes had a surface area of 16 cm$^2$ and were prepared by thermal decomposition of titanium ethoxide [Ti(OC$_2$H$_5$)$_4$] on the surface of Ti sheets (Siber Hegner Rohstoff AG, Zurich, Switzerland ASTM grade 2, thickness 0.05 cm). Exact experimental details of this preparation are described elsewhere.\(^2\) We present here preliminary results where desorption of the agent at various reaction times and spectral analysis was used to monitor degradation. More detailed kinetic evaluation for the various systems is forthcoming. However, it is obvious from the spectra illustrated in Figs. IV, and V that degradation does take place and that this decomposition is enhanced in the presence of oxidants such as K$_2$S$_2$O$_8$ and H$_2$O$_2$.

Pursuits in the immediate future involve the confirmation of these thermal degradation studies in order to optimize the reaction conditions. Other combinations of redox catalysts and strong oxidants will be tested and optimized. In addition to this experimentation, photoelectrochemical studies are underway in order to further elucidate the role of surface species (supposedly surface peroxos)\(^3\) in the mechanism of the oxidation of these CW simulants.

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FIGURE LEGENDS

Fig. I Effect of Fe$_2$(SO$_4$)$_3$ Concentration on 4-NPIPP Thermal Degradation by H$_2$O$_2$ in Aqueous Colloidal TiO$_2$ Suspensions:
[TiO$_2$] = 5 gm/l, [H$_2$O$_2$] = 3.10$^{-1}$M
[4-NPIPP] = 6.5.10$^{-4}$M; ▲ [Fe$_2$(SO$_4$)$_3$] = 5.10$^{-4}$M,
◇ [Fe$_2$(SO$_4$)$_3$] = 10$^{-3}$M, □ [Fe$_2$(SO$_4$)$_3$] =5.10$^{-3}$M
* [Fe$_2$(SO$_4$)$_3$] = 10$^{-2}$M, •[Fe$_2$(SO$_4$)$_3$] = 0, T = 50°C

Fig. II Effect of H$_2$O$_2$ concentration on 4-NFIPP Thermal Degradation with Fe$_2$(SO$_4$)$_3$ Catalyst in Aqueous Colloidal TiO$_2$ Suspensions:
[TiO$_2$] = 5 gm/l, [Fe$_2$(SO$_4$)$_3$] = 10$^{-3}$M, [4-NPIPP] = 6.5.10$^{-4}$M;
○ [H$_2$O$_2$] = 2.10$^{-2}$M, ▲ [H$_2$O$_2$] = 5.10$^{-2}$M, ◇ [H$_2$O$_2$] = 10$^{-1}$M
□ [H$_2$O$_2$] = 3.10$^{-1}$M, * [H$_2$O$_2$] = 5.10$^{-1}$M, ★ [H$_2$C$_2$] = 1M,
T = 70°C

Fig. III Effect of H$_2$O$_2$ Concentration on 4-NPIPP Thermal Degradation with Fe$_2$(SO$_4$)$_3$ Catalyst in Aqueous Solution:
[Fe$_2$(SO$_4$)$_3$] = 10$^{-3}$M, [4-NPIPP] = 6.5.10$^{-4}$M, [H$_2$O$_2$] = 2.10$^{-2}$M,
▲ [H$_2$O$_2$] = 5.10$^{-2}$M, ◇ [H$_2$O$_2$] = 10$^{-1}$M.
□ [H$_2$O$_2$] = 3.10$^{-1}$M, * [H$_2$O$_2$] = 5.10$^{-1}$M,
★ [H$_2$O$_2$] = 1M, •[H$_2$O$_2$] = 0, T = 70°C.

Fig. IV Photodecomposition of 4-NPDEP on Oxidant Coated TiO$_2$ Fractal Films: [4-NPDEP] = 1 monolayer, [K$_2$S$_2$O$_8$] = 20 monolayers, 16 cm$^2$ metal electrode, λ ≥ 350 nm (solar simulator).

Fig. V Photodecomposition of 4-NPDEP on Oxidant Coated TiO$_2$ Fractal Films: [4-NPDEP] = 1 monolayer, dipped into H$_2$O$_2$ (2 M), 16 cm$^2$ metal electrode, λ ≥ 350 nm (solar simulator).
EFFECT OF Fe CONCENTRATION ON 4-NPIPP THERMAL DEGRADATION

reaction temperature = 50°C

Tio₂, P25 5g/l, 0.3M H₂O₂

6.5E-4M 4-NPIPP

Figure 1

$\text{CO}_2$ PRODUCED (moles)/10^-5

TIME (MIN)
EFFECT OF H₂O₂ CONCENTRATION ON 4-NPIPP THERMAL DEGRADATION

reaction at 70°C

(CO₂ PRODUCED (moles))/10⁻⁵

TIME (min)

- 0.02M H₂O₂
- 0.05M H₂O₂
- 0.10M H₂O₂
- 0.30M H₂O₂
- 0.50M H₂O₂
- 1.00M H₂O₂

TiO₂, P25 5g/l
1E-3M Fe₂(SO₄)₃
6.5E-4M 4-NPIPP
Figure III

Effect of H₂O₂ Concentration on 4-NPIPP Thermal Degradation

![Graph showing the effect of H₂O₂ concentration on 4-NPIPP thermal degradation. The graph plots CO₂ produced (moles) × 10⁻⁵ against time (min) for different concentrations of H₂O₂: 0.02M, 0.05M, 0.10M, 0.30M, and 1.00M. The graph also indicates a reaction at 100°C.](image-url)