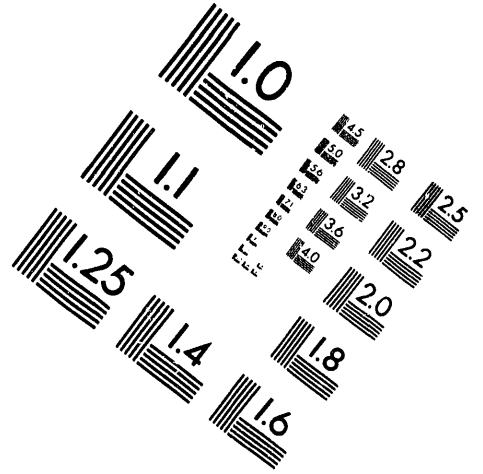
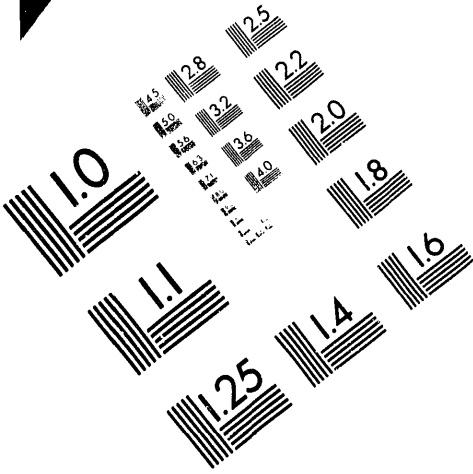




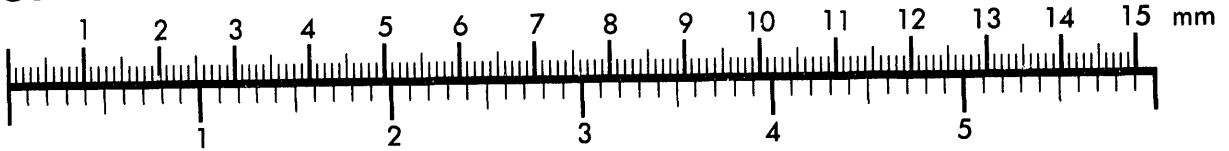
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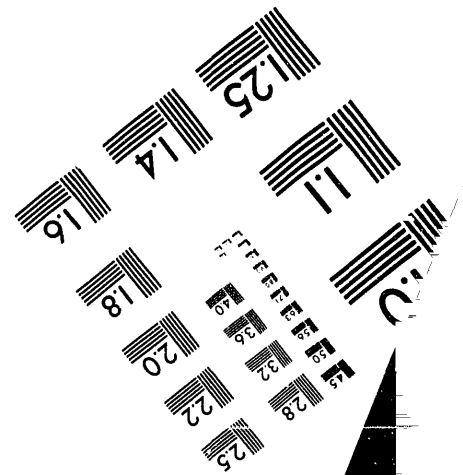
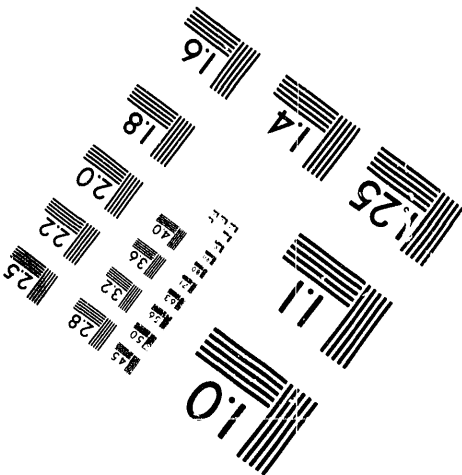
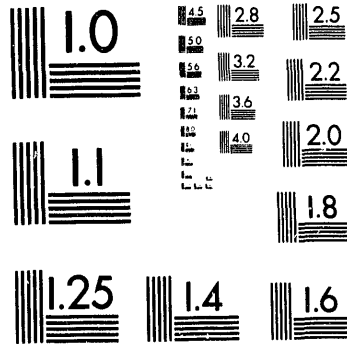
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Title: KINETIC STUDIES OF ELECTROCHEMICAL GENERATION OF Ag(II) ION AND CATALYTIC OXIDATION OF SELECTED ORGANICS

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KINETIC STUDIES OF ELECTROCHEMICAL GENERATION OF AG(II) ION AND CATALYTIC OXIDATION OF SELECTED ORGANICS

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INTRODUCTION

The goal of this research is to develop a method to treat mixed hazardous wastes containing selected organic compounds and heavy metals, including actinide elements. One approach is to destroy the organic via electrochemical oxidation to carbon dioxide, then recover the metal contaminants through normally accepted procedures such as ion exchange, precipitation, etc.

Recently, much attention has been given to the destruction of organics by exhaustive oxidation up to carbon dioxide¹⁻³. Much is known about the electrochemical behavior of many organic compounds especially with regard to reaction kinetics, mechanistic pathways and electrosynthesis. Indeed it is this wealth of chemical literature that suggests that there is no one set of reaction conditions that will be optimal for the destruction of all organic compounds. Each compound or class of compounds will have its own unique set of reaction parameters.

With this in mind we have chosen to study the electrochemical oxidation of a simple alcohol, iso-propanol. Since this compound contains only three carbon atoms, the reaction intermediates in going to carbon dioxide will most likely contain only one, two or three carbons, which should make them easy to identify and quantitate. However, the overall oxidation of iso-propanol to carbon dioxide is an 18 electron transfer process so there is still considerable complexity involved.

Much of the recent work reported involved the use of an electron transfer mediator, usually the silver(I)/(II) redox couple. This involved direct electrochemical generation of the mediator at the anode of a divided cell followed by homogeneous reaction of the mediator with the organic compound. In this study we have sought to compare the mediated reaction with direct electrochemical oxidation of the organic. In addition to silver(I)/(II) we also looked at the cobalt(II)/(III) redox couple. In the higher oxidation

state both of these metal ions readily hydrolyze in aqueous solution to ultimately form insoluble oxides. Thus all measurements were carried out in highly acid media, 6 M HNO_3 , in order to slow down the hydrolysis reaction. The non-mediated electrolysis was also done in acidic media for purpose of a direct comparison.

EXPERIMENTAL

Our experimental system consists of an electrochemical cell (H-cell with membrane or frit, platinum electrodes) connected to an optical flow cell. As a mediator is generated at the anode surface, the anolyte is pumped through the flow cell. In this way we can observe the generation of the mediator in real time using a diode array spectrophotometer. When organics are present, anolyte samples are taken and injected directly into a gas chromatograph for qualitative and quantitative analyses of reaction intermediates and products. Electrolyses were carried out to 100% theoretical completion (Ag, Co) or 100% and 50% theoretical completion (iso-propanol).

RESULTS AND DISCUSSION

In acid solution Ag(I) is oxidized at a potential slightly less positive than the solvent itself while Co(II) is oxidized at a potential slightly more positive than the solvent. Therefore it is impossible to generate Co(III) without simultaneous oxidation of the solvent. For both catalysts, it was necessary to optimize the electrolysis conditions (current density, temperature, separator) to allow for maximum catalyst generation with minimal solvent oxidation. This was done by measuring the electrogenerated Ag(II) or Co(III) concentration spectrophotometrically as previously described. As expected, for both catalysts, the generation efficiency decreased as the current density increased due to the increased significance of solvent oxidation. At elevated temperatures the rate of reduction of the catalyst by the solvent was increased thereby decreasing the current efficiency. This effect was more pronounced for the generation of Ag(II) (Fig. 1). Additionally both catalysts were generated more efficiently when a ceramic frit was used as a separator as opposed to a cation exchange membrane (Fig.2). This observation could result from many parameters (the resistance of the separator, and the flow of cations across the separator, for example) and must be investigated further.

Studies done with iso-propanol present showed that with or without the mediator present iso-propanol is readily oxidized to acetone, a stable intermediate, in a two electron transfer process. Further oxidation yields acetic acid and most likely methanol (Fig.3). The acetic acid is readily observed in the chromatogram, due to its stability toward further oxidation, while there is no trace of methanol. This is probably due to its immediate further oxidation to formaldehyde, formic acid and ultimately carbon dioxide. A general reaction sequence is presented (Fig. 4).

The oxidation of the starting alcohol and ketone intermediate are both quite rapid. It might be expected then that oxidation of the intermediate alcohol and carbonyl compound, methanol and formaldehyde would also be kinetically fast. By analogy oxidation of formic acid would be predicted to be the slow step in oxidation of methanol to carbon dioxide, just as oxidation of acetic acid appears to be rate determining. Formic acid does in fact appear in the chromatogram while there does not appear to be a significant accumulation of methanol or formaldehyde.

A potential side reaction involving two intermediates is the acid catalyzed esterification of acetic acid with methanol to form methyl acetate. Methyl acetate would also be expected to be resistant to further oxidation and should appear in the chromatogram if it is generated. The fact that it does not is due to the rapid rate at which methanol is removed from the reaction mixture through further oxidation.

The results obtained in this study indicate that only one of the carbon atoms in iso-propanol is oxidized to carbon dioxide under these reaction conditions. The remaining two carbons go to form acetic acid, a stable intermediate. To verify this we started with a solution containing only acetic acid and electrolyzed to the equivalent of approximately ten electrons per acetic acid molecule. At the end of the electrolysis there was no change from the original acetic acid concentration. It has been found by earlier researchers that the adsorption of carboxylic acids on platinum is a reversible process which makes electrooxidation of the acid difficult, though degradation of the acid is still possible at highly positive potentials.⁴ We have found that the oxidation of isopropanol to acetic acid is more efficient under the following conditions: high current density, high acidity of the anolyte, and use of a cation exchange membrane. It may be that the oxidation or degradation of acetic acid may occur with higher temperatures and longer reaction times in addition to the factors listed above.

In comparing mediated electrolysis to direct electrolysis the reaction proceeds more quickly to completion in the order: Co(III) > unmediated > Ag(II) (Fig. 5). In the mediated reactions, because the metal ions can undergo deleterious side reactions with the solvent, we might expect there to be a decrease in the organic oxidation reaction efficiency. This was observed when Ag(II) was used as a mediator. The reason why efficiency with Co(III) is greater than with Ag(II) is probably due to its more positive redox potential. During formation of Co(III) only a small fraction of the total current goes to Co(II) oxidation while a much greater fraction goes toward oxidation of the solvent or to the direct electrolysis of the starting organic and its intermediates. Additionally, any Co(III) that is formed reacts slowly enough with water such that a sufficient concentration can be generated and reaction with the organic species can occur.

CONCLUSIONS

In 6 M nitric acid solution at room temperature isopropanol can be oxidized to carbon dioxide and acetic acid. Acetic acid is a stable intermediate and resists further oxidation. The presence of Co(III) enhances the rate or efficiency of the reaction.

ACKNOWLEDGEMENTS

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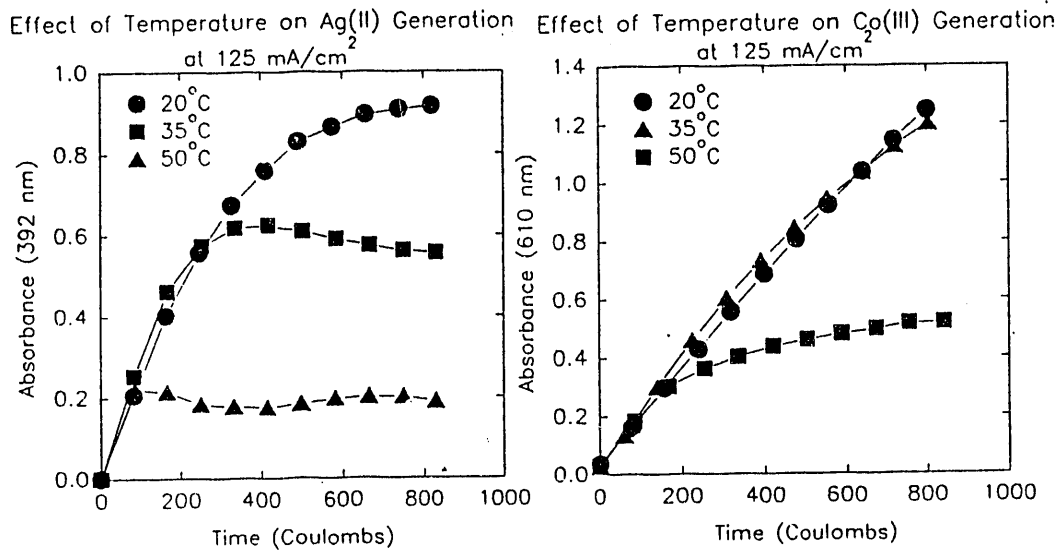


Figure 1

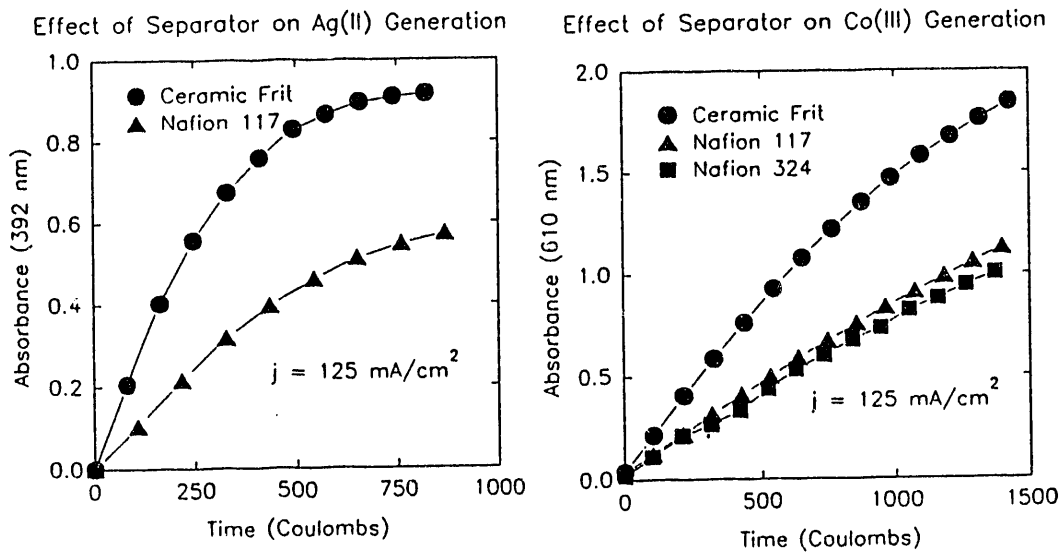


Figure 2

Destruction of Isopropanol at 500 mA/cm²

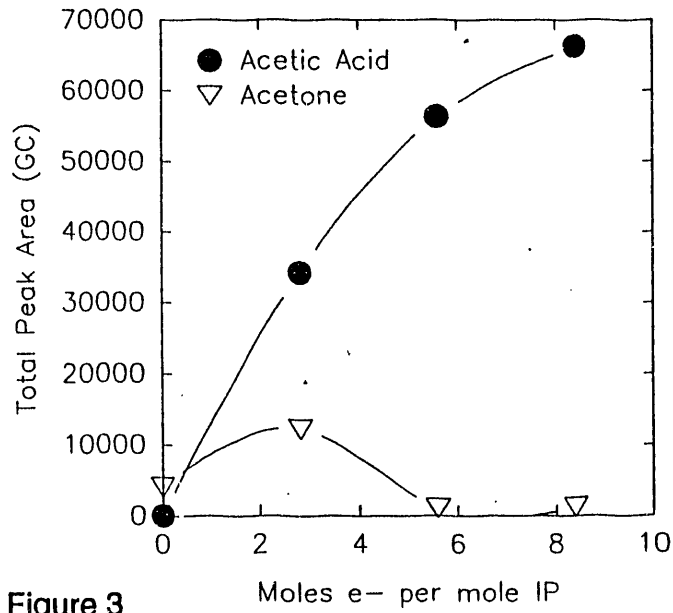


Figure 3

Effect of Catalyst on Isopropanol Destruction at 500 mA/cm²

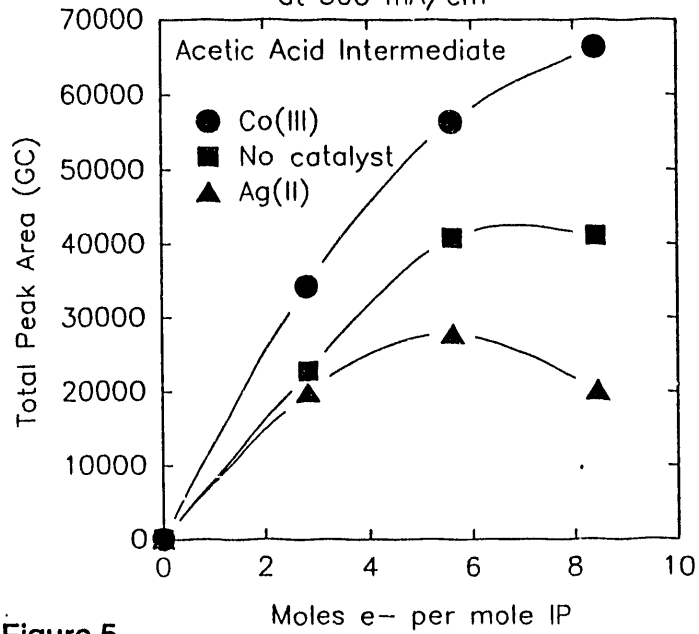


Figure 5

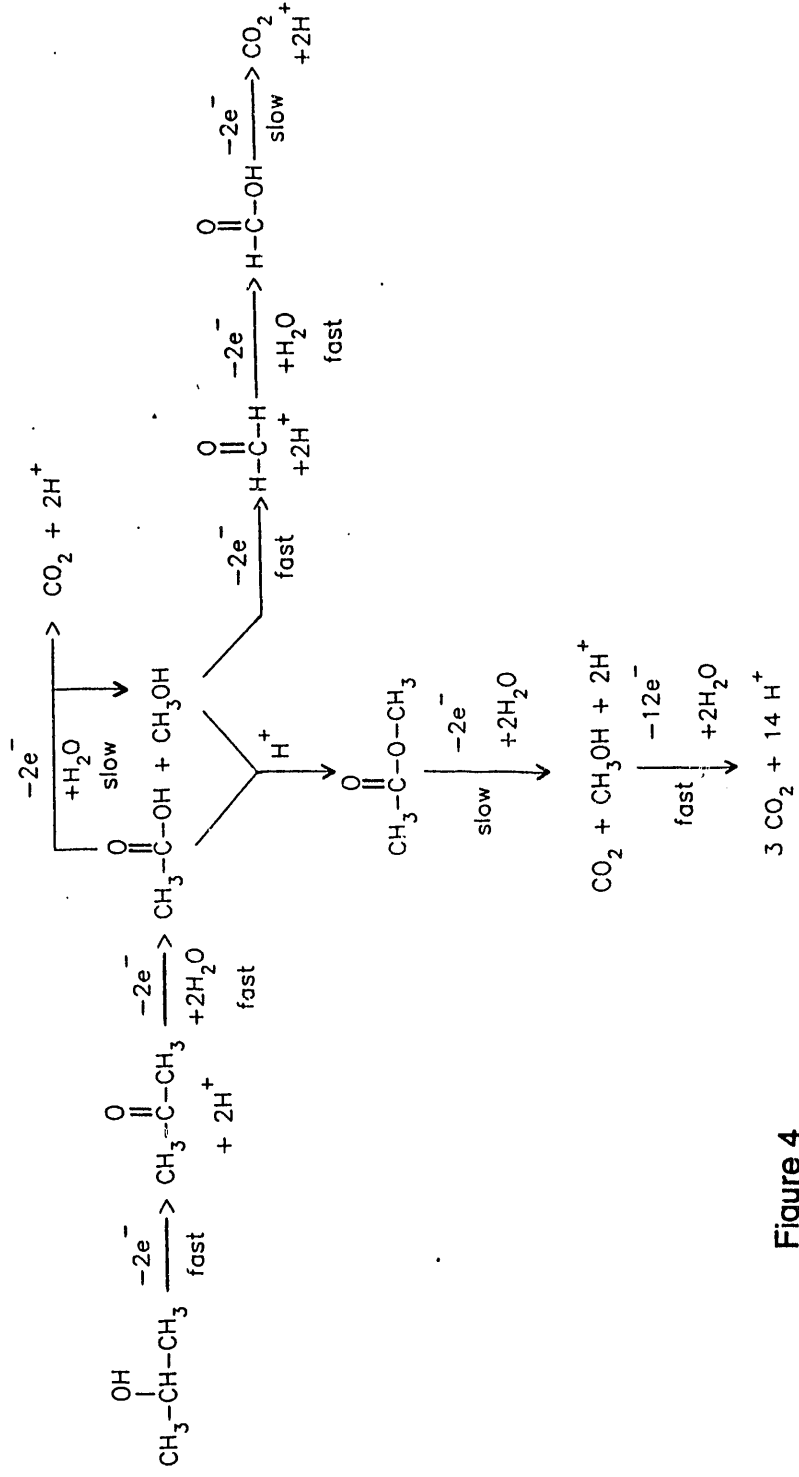
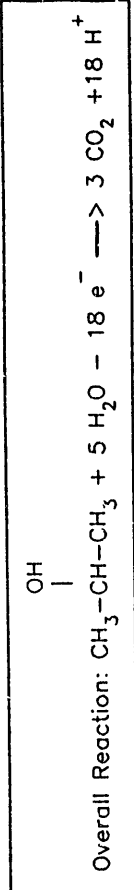


Figure 4

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