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# **SULFOXIDE AND SULFONE PREPARATIONS FROM AN AROMATIC SULFUR COMPOUND BY THE SUPEROXIDE ION GENERATED ELECTROLYCALLY FROM OXYGEN**

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The superoxide anion generated electrolytically at a mercury pool cathode was the reactant that generated sulfoxide and sulfone products from thioxanthen-9-one. When a supporting electrolyte (dodecyltrimethylammonium chloride, DTAC) was used tremendous increase in current occurred, but no sulfone or sulfoxide was generated even when the temperature was increased to 95°C. Products and reactant do not add up to 100% in every case, consequently we analyzed the reactions for the generation of carbon dioxide since the superoxide anion is known to be a strong oxidant. However, no carbon dioxide was generated from the thioxanthen-9-one.

**Keywords:** Sulfoxides; sulfones; aromatic compounds; superoxide anion oxygen; mercury pool cathode and supporting electrolyte

It is illustrated in this manuscript how an aromatic sulfur compound can be oxidized from the superoxide anion generated electrolytically at a mercury pool cathode. Both the sulfoxide and the sulfone were generated in two aprotic solvents; dimethylformamide and acetonitrile; however, the sulfone was generated only at elevated temperatures of 95°C.

Since the superoxide is known as a strong oxidant<sup>1</sup>. The electrolytic reaction was analyzed for carbon dioxide which could result if the thioxanthen-9-one were oxidized completely to carbon dioxide. Carbon dioxide was detected, but the source of the carbon dioxide was not from thioxanthen-9-one but predominately from the reaction of the superoxide anion with the carbon anode.

The carbon dioxide was removed from the electrolytic cell with nitrogen and bubbled into a standardized sodium hydroxide solution which was subsequently titrated with a standardized hydrochloric acid solution.

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## EXPERIMENTAL

### Solvents

Dimethylformamide was distilled with 20% benzene to remove the water by azeotrope with benzene between the temperature of 70° to 75°C. The dimethylformamide was collected at its boiling point of 153°C<sup>2</sup>.

Acetonitrile was distilled from anhydrous phosphorus pentoxide, and acetonitrile was collected at its boiling point of 81° to 82°C<sup>3</sup>.

### Electrolysis Cell

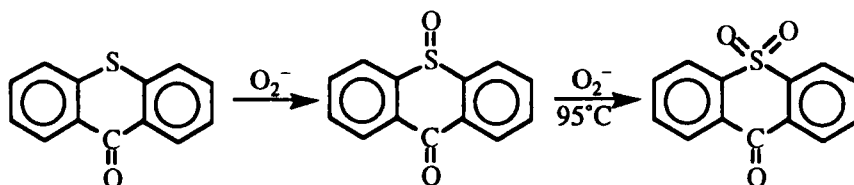
The electrolysis cell was a glass container with a diameter of 5 cm and a vertical height of 10 cm. The volume of the cell was 125 ml. A 7.5 mm diameter carbon rod served as the anode, and the bottom of the cell was filled with mercury to cover the entire bottom surface. The mercury served as the cathode. A calomel electrode served as the reference electrode. Oxygen was passed into the reaction vessel through a glass frit that was placed just above the surface of the mercury. Bath temperatures were maintained by placing the electrolytic cell in an oil bath placed on top of a heating plate.

### Potentiostat

The voltage was controlled at -1.36 volts by a Princeton Applied Research Model 362 potentiostat.

Analyses were performed on a Hewlett Packard model 1090 high-pressure liquid chromatography (HPLC) utilizing toluene as the internal standard with the uv lamp set at 250 nm. The column was a C-18 column, 1.4 inch by 12 inches. After the reaction was complete, the electrodes were washed with water and the water and DMF, and water and acetonitrile were extracted three times with approximately 50 mL of ether. A 5 mL sample of the ether extract, approximately 150 mL, was treated with 100 µL of toluene as the internal standard. Standard solutions of starting material and the sulfone and sulfoxide of thioxanthene-9-one, were also prepared with 100 µL of toluene in 5 mL of the standard and starting material. These standards and starting material were used to determine the amount of starting material recovered, and the amount of thioxanthene-9-one sulfoxide and of sulfone produced.

*High Pressure Liquid Chromatograph*—the HPLC was used to quantitatively determine the thioxanthene-9-one, and its sulfone and sulfoxide. After the elec-



trolytic reactions, the water added to the solutions and they were extracted three times with approximately 50mL of ether per extraction.

A 5mL solution of ether extract had 100 $\mu$ L of toluene added as the internal standard. Quantitative results were obtained from standard solutions of the thioxanthen-9-one, the sulfone and the sulfoxide treated with the same amount of the internal standard, toluene. Accuracy of this method was ascertained by comparing two standard solutions which gave less than 2 percent error.

### Preparation of Sulfone and Sulfoxide

The sulfone of thioxanthen-9-one was prepared from 2.8 mL of 30% hydrogen peroxide (4) dissolved in 3.8 mL of glacial acetic acid with 1 g. of thioxanthen-9-one added. The solution was boiled for one-half hour and then cooled. After cooling crystals were formed which were recrystallized from methylene chloride m.p.  $184-186^\circ$ . Mass spectrum revealed that these crystals were the sulfone crystals.

The sulfoxide of thioxanthen-9-one was prepared from the oxidizing agent, meta-chloroperbenzoic acid (4). The meta-chloroperbenzoic acid (98 mg) was dissolved in 7.5 mL of methylene chloride and dropped into a solution of 108 mg of thioxanthen-9-one dissolved in 5.0 mL of methylene chloride. The solution was stirred overnight in a refrigerator at  $8^\circ C$ . The solution was then extracted three times with sodium bicarbonate. The solvent was dried with anhydrous magnesium sulfate and evaporated to dryness. Crystals were recrystallized from n-hexane and the mass spectrum revealed the crystals were the sulfoxide compound.

## RESULTS AND DISCUSSION

The superoxide ion has been generated electrolytically to produce sulfoxide and sulfone from the aromatic sulfur compound thioxanthen-9-one. In Table I are listed the reactions of thioxanthen-9-one at different temperatures with and without the supporting electrolyte.

TABLE I Reaction of thioxanthone with and without DTAC\*

Thioxanthone (mg)	Conc. DTAC* (mmoles)	Solvent (50 mL)	Temp. (°C)	% Sulfoxide	% Sulfone	% Thioxanthene recovered	Time of Rx (hrs)
100.9	7.2	CH <sub>3</sub> CN	Rm. Temp.	0	0	100	23
102.0	7.2	CH <sub>3</sub> CN	Rm. Temp.	0	0	100	22
100.9	7.2	DMF	95°	0	0	100	16.5
103.0	7.2	DMF	95°	0	0	100	16.0
103.1	0	CH <sub>3</sub> CN	Rm. Temp.	19.8	0	81	18.0
103.1	0	CH <sub>3</sub> CN	Rm. Temp.	17.1	0	82.5	18.2
101.5	0	DMF	98°	12.7	8.8	54.1	12
103.9	0	DMF	94°	16.3	25.5	28	12.5
109.7	0	DMF	95°	16.9	8.2	72	9

\*DTAC—Dodecyltrimethylammonium chloride

The analysis with and without the supporting electrolyte, dodecyltrimethylammonium chloride (DTAC), produced some interesting results. With the supporting electrolyte no sulfone or sulfoxide was produced regardless of whether the temperature was at room temperature or 95°C. Undoubtedly, the reason for this is that the supporting electrolyte was attached to the superoxide anion and preventing it from attacking the sulfur linkage in the aromatic compound.

As Table I also reveals, no sulfone is produced at room temperature with the solvent acetonitrile. This was not surprising because sulfoxides and sulfones can be prepared from the peroxide anion and the sulfone preparation requires a temperature above 100°(5).

Table I also reveals that in some cases the sulfone, sulfoxide and starting material recovered did not add up to 100%. It was of interest to determine if the superoxide ion was oxidizing any of the thioxanthene-9-one to carbon dioxide.

The outlet from the electrolytic cell, was connected having been purged with nitrogen, to a standardized sodium hydroxide solution apparatus (Figure 1). It was found that carbon dioxide was generated from the electrolysis apparatus.

To have a valid measurement of carbon dioxide from these electrolytic reactions it must be determined if carbon dioxide could result from the carbon electrode and/or the reaction with the surfactant, dodecyltrimethylammonium chloride (DTAC).

After an electrolytic reaction was run, approximately one and one-half mL of concentrated hydrochloric acid was added to the reaction vessel, and the flask was degassed with nitrogen for one hour. The nitrogen passed into the second vessel through a medium glass frit into a standard solution of sodium hydroxide.

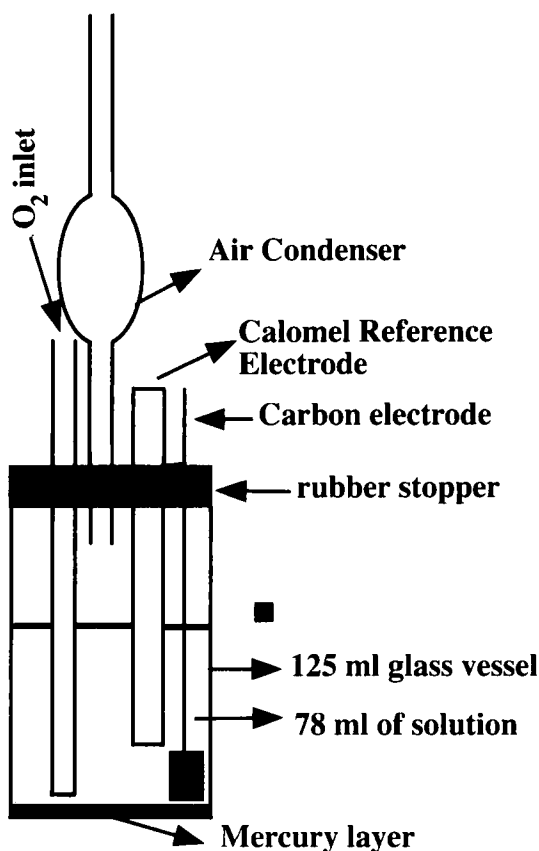


FIGURE 1 The Electrolysis Cell.

After precipitating the carbonate ions with excess barium chloride, the sodium hydroxide was back titrated with standardized hydrochloric acid to determine the amount of carbon dioxide produced in the reactions (6). To ascertain if the apparatus was performing properly, blank runs with anhydrous sodium carbonate were run and 99% plus of carbon dioxide was recovered with the blanks.

To determine the amount of carbon dioxide produced from the carbon electrode, two platinum electrodes were used to establish a background level for carbon dioxide. These results are shown in Table II. With the electrolysis set at  $-1.36$  V and only DTAC present,  $0.025$  M of carbon dioxide was formed which would represent the background level of carbon dioxide from the experimental procedure.

TABLE II Carbon dioxide generation from electrolysis

<i>a. Carbon Dioxide Measurements at -1.36 volts with Pt vs. Pt Electrodes</i>		
<i>Electrolysis Duration (hrs)</i>	<i>mmoles of CO<sub>2</sub> produced</i>	<i>Electrolyte (mmoles)</i>
24	0.025	DTAC (7.2 mmoles)
24	0.025	DTAC (7.2 mmoles)
<i>b. Carbon Dioxide Measurements at -1.36 volts with Hg Pod Electrode vs. Carbon Anode</i>		
<i>Electrolysis Duration (hrs)</i>	<i>mmoles of CO<sub>2</sub> produced</i>	<i>Electrolyte (mmoles)</i>
24	0.05	DTAC (7.2 mmoles)
24	0.05	DTAC (7.2 mmoles)

To ascertain if any carbon dioxide was generated from the carbon anode we performed the same procedure as above was performed with a Hg pool electrode and a carbon anode with the voltage set at  $-1.36$  V in the presence of DTAC. The carbon dioxide did increase by 100 percent over the platinum electrodes. These results are also shown in Table II.

In conclusion, one can say that the superoxide anion made from molecular oxygen by reduction at a mercury cathode can convert thioxanthen-9-one to sulfoxide at room temperature and to the sulfone at elevated temperatures. The superoxide is a strong oxidizing agent, however, no evidence of oxidation to the carbon dioxide product was detected by the carbon dioxide measurements.

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