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ELECTROCHEMICAL STUDIES OF SULFUR OXYCHLORIDES(U) STATE 1/1

UNIV OF NEW YORK AT BUFFALO DEPT OF CHEMISTRY

R A OSTERYOUNG ET AL. 28 MAR 88 ARO DRAG29-83-N-0096

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







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ELECTROCHEMICAL STUDIES OF SULFUR OXYCHLORIDES

FINAL REPORT

ROBERT A. OSTERYOUNG AND JANET G. OSTERYOUNG

MARCH 28, 1988

U.S. ARMY RESEARCH OFFICE

CONTRACT DAAG29-83-K-0096

DEPARTMENT OF CHEMISTRY  
STATE UNIVERSITY OF NEW YORK AT BUFFALO  
BUFFALO, NEW YORK 14214

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION <b>Unclassified</b>		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited.	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		4. PERFORMING ORGANIZATION REPORT NUMBER(S)	
4. PERFORMING ORGANIZATION REPORT NUMBER(S)		5. MONITORING ORGANIZATION REPORT NUMBER(S) <b>ARO 19436.3-CH</b>	
6a. NAME OF PERFORMING ORGANIZATION Department of Chemistry State University of New York	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION U. S. Army Research Office	
6c. ADDRESS (City, State, and ZIP Code) Buffalo, New York 14214		7b. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION U. S. Army Research Office	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER <b>DAAG29-83-K-0096</b>	
8c. ADDRESS (City, State, and ZIP Code) P. O. Box 12211 Research Triangle Park, NC 27709-2211		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO	PROJECT NO
		TASK NO.	WORK UNIT ACCESSION NO
11. TITLE (Include Security Classification) <b>ELECTROCHEMICAL STUDIES OF SULFUR OXYCHLORIDES (Unclassified)</b>			
12. PERSONAL AUTHOR(S) <b>Robert A. Osteryoung and Janet G. Osteryoung</b>			
13a. TYPE OF REPORT <b>Final</b>	13b. TIME COVERED FROM <b>6/83</b> TO <b>12/87</b>	14. DATE OF REPORT (Year, Month, Day) <b>1988, March 28</b>	15. PAGE COUNT <b>11</b>
16. SUPPLEMENTARY NOTATION The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	Thionyl chloride, pulse voltammetry, dimethylformamide, electrochemistry, coulometry, nuclear magnetic resonance	
19. ABSTRACT (Continue on reverse if necessary and identify by block number)			
<p>The electrochemistry of thionyl chloride has been studied at glassy carbon electrodes in dimethylformamide with tetrabutylammonium hexafluorophosphate as supporting electrolyte. Techniques employed were normal and reverse pulse voltammetry, rotating ring-disk voltammetry, coulometry and NMR. The reactions taking place during the reduction of <math>\text{SOCl}_2</math> in DMF are probably best represented by the solvation reaction,</p> $\text{SOCl}_2 + 2\text{DMF} \rightleftharpoons \text{SO} \cdot 2\text{DMF} + 2\text{Cl}^-$ <p>and the electrochemical reduction,</p> $\text{SO} \cdot 2\text{DMF} + 2e^- \rightleftharpoons \text{SO}^- \cdot 2\text{DMF}$ <p>where the product, <math>\text{SO}^-</math>, may be solvated by DMF and can be reoxidised back to the initial reactant.</p>			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION <b>Unclassified</b>	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

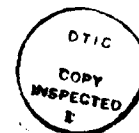
## STATEMENT OF PROBLEM

The goal of this research was to study the fundamental electrochemistry of thionyl and sulfuryl chlorides utilizing pulse voltammetric and other electrochemical techniques, and fourier transform spectroelectrochemistry. It had been proposed to study sulfuroxyhalides (1) as solutes in a non-aqueous solvent, (2) undiluted, employing lithium tetrachloroaluminate and (3) as a major component in a mixed solvent with other non-aqueous solvents.

However, due to significant problems associated with this research, only item (1) was carried to completion. A rather detailed study of the reduction of thionyl chloride in dimethylformamide was carried out. The results, summarized below, represent new and novel findings when compared and contrasted to past work in this area.

## SUMMARY OF RESULTS

In the initial phases of this work, controlled potential coulometry and rotating ring-disk electrode voltammetry for the reduction of  $\text{SOCl}_2$  were carried out at glassy carbon electrodes in *N,N*-dimethylformamide (DMF) with tetra-butylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) as supporting electrolyte. Cyclic voltammetry showed only one reduction wave for  $\text{SOCl}_2$  in DMF, as opposed to other reports which have indicated several reduction waves at platinum electrodes. During the initial phases of the electrolysis, coulometry yielded an  $n$  value of two electrons per molecule of  $\text{SOCl}_2$  reduced. During the latter phase of electrolysis, a value of  $n$  greater than two was obtained, Figure



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1. Cyclic voltammetry on the solution during electrolysis showed the presence of additional electroactive products which formed as the electrolysis progressed (Figure 2). Normal pulse voltammetric analysis of solutions containing thionyl chloride showed two chloride ions formed in solution for each molecule of  $\text{SOCl}_2$  added to solution or reduced (Figure 3). The two electron product of the reduction was examined by rotating ring-disk voltammetry (Figure 4). The product is reasonably stable in DMF, as indicated by both the results of the coulometry and by the ring-disk studies, and can be reoxidized irreversibly, also in a two-electron process, as shown by the results of Table I which present data for the ring collection efficiency,  $N$ , yielding a mean value  $1/N$  of 2.74, compared to a theoretical value, based solely on the ring-disk geometry, of  $1/N = 2.6$ . Thus, thionyl chloride in DMF was found to reduce in a two electron process at a glassy carbon electrode and yield a product, "SO", which could be reoxidized, also in a two electron process.

In a second phase of the work, normal and reverse pulse voltammetry were used to investigate both the reduction and oxidation of  $\text{SOCl}_2$  at glassy carbon electrodes in DMF with  $\text{TBAPF}_6$  as supporting electrolyte and NMR spectroscopy was used to probe for specific interactions between  $\text{SOCl}_2$  and DMF. NMR spectra and the quantitative treatment of normal and reverse pulse voltammograms gave evidence for the displacement of  $\text{Cl}^-$  in  $\text{SOCl}_2$  by DMF. The addition of  $\text{AgNO}_3$  to the solution was found to remove chloride; i.e., the oxidation wave observed which corresponds to chloride oxidation diminished, while the  $\text{SOCl}_2$  reduction wave was not affected (Figure 5, Figure 6). NMR

spectra showed evidence of a specific interaction between  $\text{SOCl}_2$  and DMF (Figure 7, Table II). The reactions taking place during the reduction of  $\text{SOCl}_2$  in DMF are probably best represented by the solvation reaction,



and the electrochemical reduction,



where the product, "SO", may be solvated by DMF and can be reoxidized back to the initial reactant. Analysis of normal pulse voltammograms for the  $\text{SO}^{2+}$  reduction indicate that the rate-determining step is a one-electron transfer, and there is no evidence for an intermediate in the overall electroreduction to "SO". It appears that "SO" species reacts further in a following chemical reaction at long pulse times and high concentrations of  $\text{SOCl}_2$ . The oxidations of both "SO" and  $2\text{Cl}^-$  are irreversible and involve two electrons.

#### PUBLICATIONS

"The Cathodic Reduction of  $\text{SOCl}_2$  in N,N-dimethyl Formamide. I. Controlled Potential Coulometry and Rotating Ring-Disk Electrode Voltammetry", Masanori Sakai, Janet Osteryoung and Robert A. Osteryoung, Journal of the Electrochemical Society, in press.

"Pulse Voltammetric and NMR Investigations of  $\text{SOCl}_2$  in N,N-Dimethyl Formamide", Winston Go, Masanori Sakai, Thomas Zawodzinski, Janet Osteryoung and Robert A. Osteryoung, Journal of Physical Chemistry, in press.

(reprints of these papers and DD-1473's will be forwarded when received)

#### PARTICIPATING SCIENTIFIC PERSONNEL

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Dr. Winston Go\*

Dr. John O'Dea\*

Mr. Thomas Zawodzinski\*\*

\* Post-doctoral Fellow

\*\* Graduate Student

Table I The ratio  $-i_{\text{disk}}/i_{\text{ring}}$  measured at various potentials and rotation rates of the electrode for various concentrations of  $\text{SOCl}_2$  containing 0.3 M TBAPP<sub>6</sub> in DMF at 27°C

Rotation rate, rpm	0.3 mM $\text{SOCl}_2$						0.8 mM $\text{SOCl}_2$					
	$E_p, V$	-0.775	-0.825	-0.875	-0.925	-1.025	-0.75	-0.775	-0.825	-0.875	-0.925	-1.025
250	2.65	2.72	2.73	2.70	2.76	2.62	2.60	2.63	2.66	2.68	2.69	
500	2.68	2.68	2.71	2.75	2.74	2.60	2.61	2.65	2.67	2.66	2.68	
750	2.72	2.73	2.73	2.72	2.74	2.60	2.60	2.67	2.65	2.68	2.67	
1000	2.68	2.69	2.71	2.77	2.75	2.62	2.62	2.65	2.67	2.69	2.62	
1500	2.74	2.72	2.73	2.74	2.78	2.64	2.63	2.66	2.68	2.69	2.68	
2000	2.71	2.75	2.74	2.75	2.77	2.61	2.67	2.67	2.69	2.70	2.60	
3000	2.77	2.76	2.75	2.76	2.78	2.64	2.64	2.67	2.68	2.71	2.70	
4000	2.76	2.79	2.79	2.78	2.78	2.63	2.64	2.66	2.69	2.71	2.70	

Rotation rate, rpm	2 mM $\text{SOCl}_2$						3 mM $\text{SOCl}_2$						
	$E_p, V$	-0.750	-0.775	-0.825	-0.875	-0.925	-1.025	-0.750	-0.775	-0.825	-0.875	-0.925	-1.025
250	2.73	2.70	2.70	2.68	2.70	2.68	2.62	2.66	2.63	2.68	2.68	2.68	2.59
500	2.65	2.69	2.68	2.70	2.68	2.69	2.65	2.68	2.69	2.69	2.70	2.74	2.74
750	2.65	2.71	2.68	2.69	2.72	2.70	2.63	2.71	2.69	2.73	2.74	2.72	2.72
1000	2.70	2.71	2.68	2.69	2.72	2.70	2.68	2.71	2.74	2.74	2.74	2.74	2.77
1500	2.70	2.73	2.70	2.69	2.70	2.71	2.70	2.73	2.72	2.75	2.76	2.77	2.77
2000	2.71	2.67	2.69	2.70	2.70	2.71	2.73	2.80	2.74	2.79	2.79	2.78	2.78
3000	2.77	2.73	2.70	2.70	2.71	2.70	2.77	2.80	2.79	2.79	2.79	2.80	2.80
4000	2.75	2.72	2.68	2.69	2.73	2.73	2.78	2.84	2.84	2.81	2.80	2.83	2.83

TABLE II Summary of  $^{17}\text{O}$  NMR data for  $\text{SOCl}_2$  in DMF.

$[\text{SOCl}_2]$ (M)	Relative Intensities			Chemical Shift (ppm)		
	$I_A/I_B$	$I_A/I_C$	$(I_A/I_C)_{\text{calc.}}^a$	A	B	C
0.5	-	10.5	11.9	423.4	-	323.0
1.0	2.22	6.1	6.5	432.7	316.8	308.0
2.0	1.99	2.4	2.2	435.8	316.7	308.1

<sup>a</sup> assuming the DMF molecules are associated with each  $\text{SOCl}_2$  molecule.

## Figure Captions

Figure 1. Plot of rotating disk limiting current,  $i_d$ , vs. number of coulombs,  $Q$ , during the controlled potential reduction of 2mM  $\text{SOCl}_2$  with 0.15M  $\text{TBAPF}_6$  in DMF at 27°C.

Rotation rate of the electrode, 1000 rpm; scan rate,  $1 \text{ mV s}^{-1}$ .

○, -1.6 V; ●, -1.2 V; △, -0.7 V.

Figure 2. Cyclic voltammograms before and during controlled potential coulometry of 2 mM  $\text{SOCl}_2$  in DMF with  $\text{TBAPF}_6$  at 27°C. Scan rate,  $100 \text{ mV s}^{-1}$ .

a) before electrolysis; b)  $n=0.5(9\text{C})$ ; c)  $n=1.2(24\text{C})$ ; d)  $n=1.8(34\text{C})$ ;

(-----), background.

Figure 3. Normal pulse voltammograms of the oxidation of solutions containing a) 2 mM  $\text{SOCl}_2$ ; b) 2 mM  $\text{Cl}^-$ ; c) 2 mM  $\text{SOCl}_2$  and 2 mM  $\text{Cl}^-$  in DMF with 0.15 M  $\text{TBAPF}_6$  at 27°C. Pulse width, 40 ms; step height, 25 mV; delay before pulse, 5 s; (-----), background.

Figure 4. Reduction of 2mM  $\text{SOCl}_2$  at a glassy carbon disk electrode and corresponding oxidation current on the glassy carbon ring electrode at various rotation rates in DMF containing 0.15 M  $\text{TBAPF}_6$  at 27°C. Ring potential: +0.7 V; Scan rate;  $1 \text{ mV s}^{-1}$ . Rotation rates given on curves.

Figure 5. Normal pulse voltammograms for the (i) oxidation, and (ii) reduction of 2 mM  $\text{SOCl}_2$  0.15 M  $\text{TBAPF}_6$  in DMF with added  $\text{AgNO}_3$ .  $E_1 = -0.050$  V,  $t_p = 50$  ms,  $A = 0.071$  cm<sup>2</sup>,  $C_{\text{AgNO}_3} = 0$  (  $\circ$  ), 1 (  $\Delta$  ), 2 (  $\square$  ), 3 (  $\langle$  ), and 4 (  $\nabla$  ) mM.  $t_d = 5$  s,  $t_p = 50$  ms.

Figure 6. Normal pulse voltammetry of 2 mM  $\text{SOCl}_2$  0.15 M  $\text{TBAPF}_6$  in DMF with added  $\text{AgNO}_3$ : dependence of  $|i_{\text{NP}}|$  for the oxidation (  $\diamond$  ) and reduction (  $\circ$  ) currents on the concentration of added  $\text{AgNO}_3$ . The reduction currents are the peak currents. For the oxidation currents, slope =  $0.066 \pm 0.003$  mA/mM, intercept =  $-0.252 \pm 0.005$  mA,  $R = 0.998$ .

Figure 7. NMR spectrum of  $^{17}\text{O}$  for 2 M  $\text{SOCl}_2$  in DMF. Peaks are labelled from the furthest to the least downfield as A, B, and C respectively.

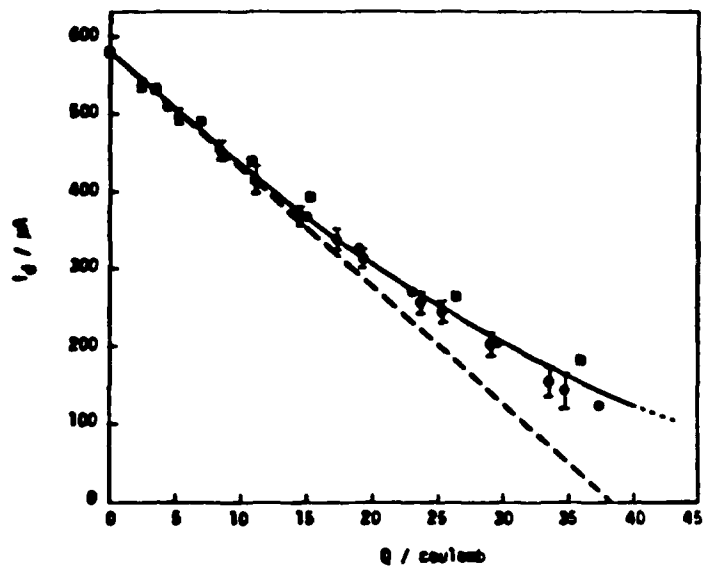


Figure 1

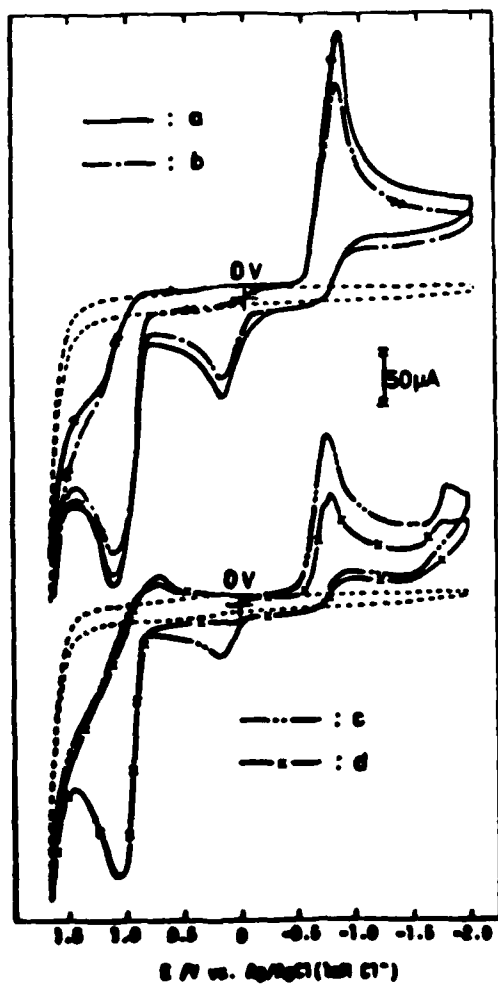


Figure 2

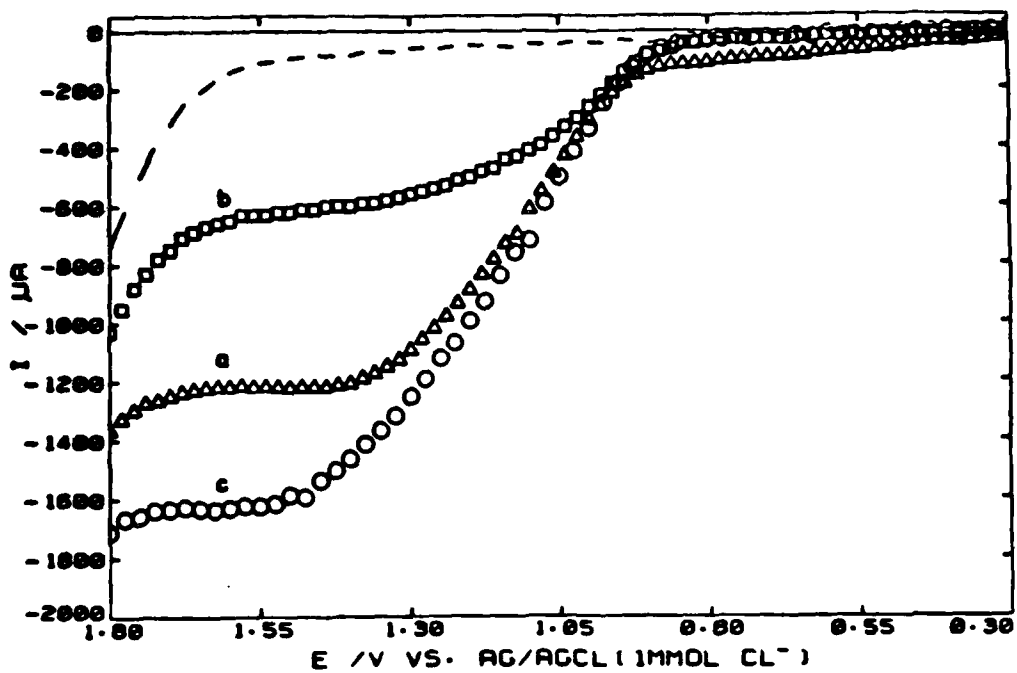


Figure 3

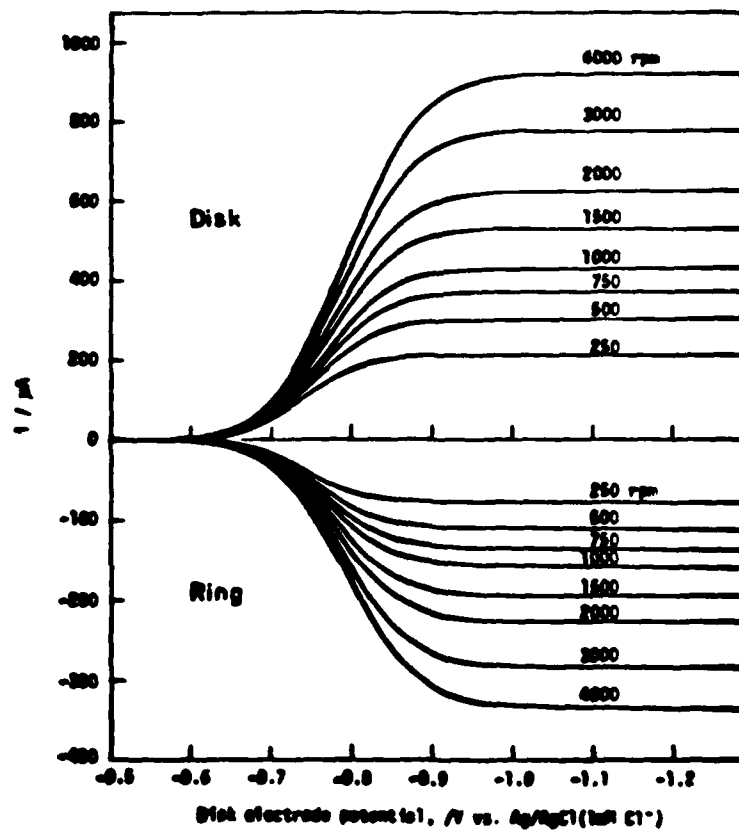


Figure 4

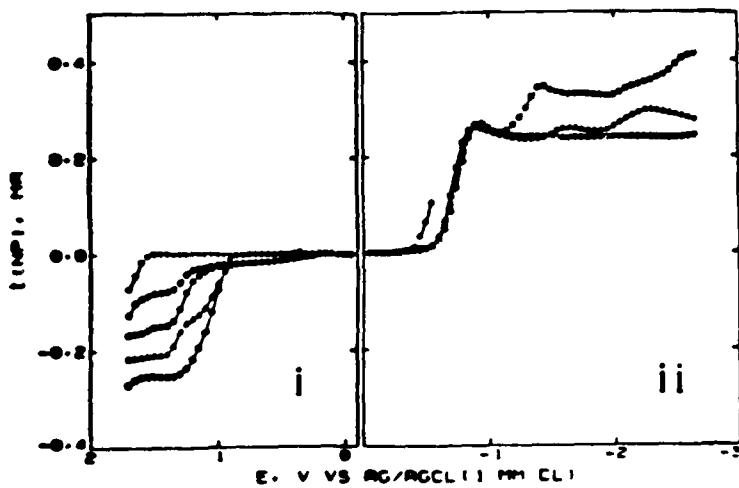


Figure 5

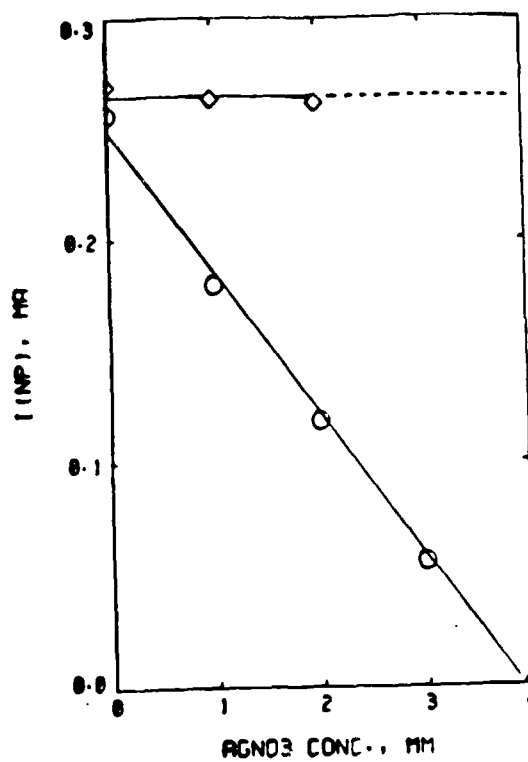


Figure 6

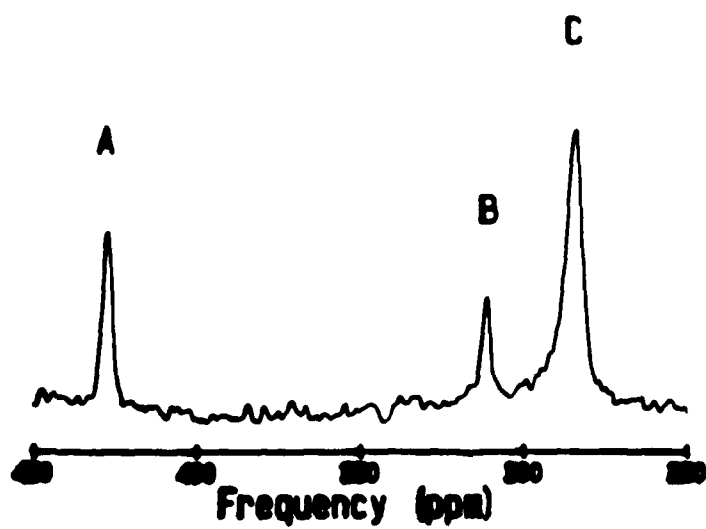


Figure 7

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