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THE ANODIC OXIDATION OF OXALIC ACID ON Au

by

JEAN LOUIS LUCIEN DESMARTIN, 1945 -

A Thesis

Submitted to the Faculty of

UNIVERSITY OF MISSOURI - ROLLA

In Partial Fulfillment of the Requirements for the

Degree of

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1970

Approved by

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THE ANODIC OXIDATION OF OXALIC ACID ON Au

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and

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ABSTRACT

The anodic oxidation of oxalic acid on Au has been studied at 25°C in aqueous media. The reaction rate was measured as a function of potential, oxalic acid concentration, pH, and temperature in $\text{H}_2\text{SO}_4\text{-K}_2\text{SO}_4$ solutions. A change in the Tafel slope in going from the lower to the higher Tafel region is explained by an alteration of the reaction mechanism due to electrical interactions between adsorbed species and the anode. Further details of an oxidation sequence involving resonant forms of oxalic acid are proposed.

INTRODUCTION

Several studies have been reported concerning the anodic oxidation of oxalic acid. Giner,¹ Llopis,² and Shams El Din³ studied the reaction on Pt at room temperature and reported a complete oxidation to CO_2 . A mechanism was proposed favoring the formation of an oxygen - containing

species which subsequently participated in the oxidation. Johnson, Wroblowa, and Bockris⁴ studied the electro-oxidation on Pt at 80°C and concluded that it occurred directly without an oxide film intermediate. A change in the Tafel slope was noted at approximately 50°C which indicated the rate determining step to change from the first charge transfer at lower temperatures to the second charge transfer at higher temperatures. Johnson, Mueller, and James⁵ studied the oxidation of oxalic acid on Au at 80°C in a potential region where the involvement of oxygen - containing species would be unlikely. A sequence proposed earlier for the reaction on Pt which did not involve oxygen - containing species was found to correlate the experimental results assuming the first decarboxylation to be rate determining.

The present study on Au at 25°C was carried out to obtain additional data that might be used to test or to give further insight into the mechanism involving the resonant form of oxalic acid proposed earlier.

EXPERIMENTAL

Cell and Apparatus

The cell, apparatus and procedures have been described previously.⁶ The anode was a 15 cm² rectangular piece of fine gold foil that was activated before each run. The reference electrode was Hg/Hg₂SO₄ (1 N H₂SO₄). All potentials are reported vs. the standard hydrogen electrode (SHE) at the temperature of the experiment. All experiments were carried out at 25±0.2°C except as noted.

Reagents

The oxalic acid, sulfuric acid, and potassium sulfate were Fisher "Certified" reagents. Matheson prepurified nitrogen was used for purging and stirring. Conductivity water was used to prepare the solutions.

RESULTS

Rest Potentials

The rest potentials were 0.47 ± 0.02 V in 1 N H_2SO_4 and independent of oxalic acid concentration. They were also relatively independent of pH over the range studied. The corresponding reversible potentials for complete conversion to CO_2 are -0.52 to -0.58 V.

Current-Potential Relationships

The polarization curves were obtained potentiostatically and points were reproducible within $\pm 10\%$. Steady currents were reached in approximately 10 minutes. Tafel plots for the various oxalic concentrations and pH's are shown in Figs. 1 and 2. The curves for the higher concentrations (0.1 and 0.3 M) contain two linear regions, each spanning approximately 1.5 decades of current, and with slopes of about 70 (2.3 RT/F) and 110 mV (2.3 RT/ α F). This effect is less obvious at lower concentrations, due to the difficulty of measuring the small currents involved. The two regions appear to be separated at a potential of ca. 0.81 V. Limiting currents were reached 1.02 V, that were of the same order of magnitude as the values observed at 80°C.

Oxalic Acid Concentration and pH Effects

The electrolytes were solutions of H_2SO_4 and/or K_2SO_4 in which the sulfate normality was held constant at

unity to insure good conductance. The necessary quantities of H_2SO_4 and K_2SO_4 for a given oxalic acid concentration and pH were calculated from equilibrium data. As with previous investigations,^{4,5} it was necessary to use the concentration of the unionized species to obtain consistent reaction orders. The concentration effect on current in 1 N H_2SO_4 is shown in Fig. 3. The reaction order is close to unity and was used to establish the concentration effect for the other pH's. Data from Fig. 3 at a constant concentration of unionized oxalic acid for the various pH's are shown in Fig. 4 and give a pH effect close to unity.

Temperature Effect

The current-temperature relations were determined potentiostatically in 1 N H_2SO_4 and are shown in Fig. 5. The apparent activation energies are 19.8 and 21.4 kcal at +0.782 and +0.702 V, respectively. The effect of potential on the activation energy, $\partial E_a/\partial V$, is ca. -20 kcal/volt, approximately that associated with the observed Tafel slope in this potential region. Using $\partial E_a/\partial V = -23$ kcal (ca. -F), the true activation energy at the reversible potential is estimated to be 48 kcal.

Coulombic Efficiency

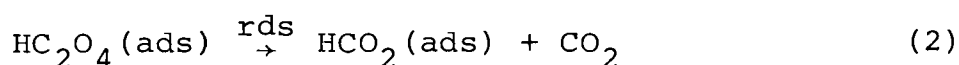
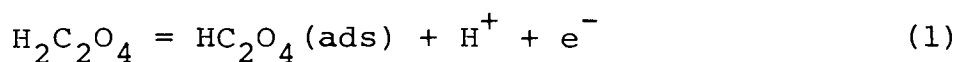
The results of the coulombic efficiency experiments are shown in Table I. Within experimental error, the conversion to CO_2 is considered complete.

TABLE I
 COULOMBIC EFFICIENCY FOR CO₂ PRODUCTION FOR THE
 ANODIC OXIDATION OF OXALIC ACID ON Au AT 25°C

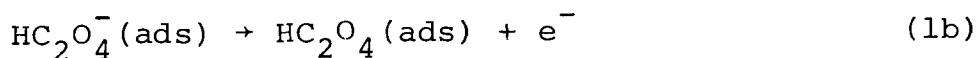
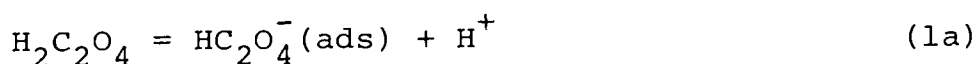
Oxalic Acid Concentration	Electrolyte pH	Current	Potential	Time	CO ₂ Produced	Efficiency
gmol/liter		ma	V	hr:min	mgm	%
0.01	0.5	2.9	0.93	18:15	92	105±10%
0.01	2.6	1.7	0.78	25:15	76	106±10%

DISCUSSION

This study at 25°C covers approximately the same range of potential as the previous study at 80°C.⁵ Therefore water discharge reactions are considered to be unlikely, even in the higher Tafel region. The kinetic parameters observed at the lower potentials are also consistent with the mechanism proposed for 80°C, i.e.,

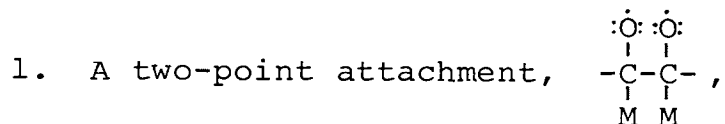


In the higher Tafel region, the Tafel slope of 110 mV indicates that the first electron transfer becomes rate determining. This can be taken into account by considering reaction (1) to consist of at least two consecutive steps:



The increased Tafel slope is observed when step 1b becomes rate determining at the higher potentials. The second electron transfer and decarboxylation occur as previously described.⁵ A schematic representation of the suggested sequence is helpful in illustrating this change of r.d.s. As suggested previously,⁵ the first

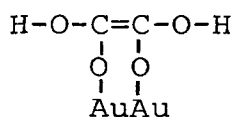
step is adsorption through resonance in the unionized species, as shown in Step I (Fig. 6). A one-point attachment is indicated by the following:



would give rise to two unpaired electrons, whereas most of free radicals have only one unpaired electron.

2. A two-point attachment would hinder the possibility of further resonance that is necessary for continued reaction.

3. An oxygen-metal attachment, as suggested for similar compounds like thiourea,⁷ would give rise to the following structure,



which is an enolic form and therefore less stable. Step II is the loss of a proton from the non-adsorbed -COOH group which can also be envisioned as occurring relatively easily.

We now must consider Steps III (the first electron transfer) and V (the first decarboxylation), which would occur with more difficulty and their relative velocities. If the species formed by Step III undergoes a further ordinary resonance in the non-adsorbed carboxylate group (Step IV), it would contain a positively charged carbon atom. The point of zero charge for gold can be presumed

to be less than 0.3 V(SHE).⁸ Therefore at the potentials of this study, a positive charge is present on the electrode. The repulsion between the carbon atom and the gold surface assists the decarboxylation and when the potential has increased sufficiently, the velocity of Step V increases to such an extent that Step III becomes rate determining.

It thus appears that a common mode of reaction is operative for the oxidation of oxalic acid on both Au and Pt at high and low temperatures. The different reaction parameters can be explained in terms of ordinary resonance phenomena and differing coverages of the adsorbed organic species that are consistent with the catalytic properties of the metals.

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Captions for Figures

- Figure 1. Current-potential relationships for the anodic oxidation of oxalic acid on Au in 1 N H_2SO_4 at 25°C. (\diamond , 0.001 M; \bullet , 0.003 M; Δ , 0.01 M; \square , 0.03 M; \circ , 0.1 M; ∇ , 0.3 M $\text{H}_2\text{C}_2\text{O}_4$).
- Figure 2. Current-potential relationships for the anodic oxidation of 0.01 M oxalic acid on Au in various $\text{K}_2\text{SO}_4 - \text{H}_2\text{SO}_4$ solutions at 25°C. (\circ , pH = 0.5; \square , pH = 1.0; ∇ , pH = 1.6; Δ , pH = 2.4).
- Figure 3. Current-unionized oxalic acid concentration relationships for the anodic oxidation of oxalic acid in various $\text{K}_2\text{SO}_4 - \text{H}_2\text{SO}_4$ solutions at 25°C and +0.752 V(SHE) (Δ , 1N H_2SO_4 , pH = 0.5; \circ , pH = 1.0; \square , pH = 1.6; ∇ , pH = 2.4).
- Figure 4. Current-pH relationship for the anodic oxidation of oxalic acid at 25°C and +0.752 V(SHE) (unionized oxalic acid concentration = 0.001 M).
- Figure 5. Current-temperature relationship for the anodic oxidation of 0.1 M oxalic acid in 1 N H_2SO_4 (∇ , V = +0.782 V(SHE); \circ , +0.702 V(SHE)).

Figure 6. Schematic representation of the mechanism of oxalic acid oxidation on Au.

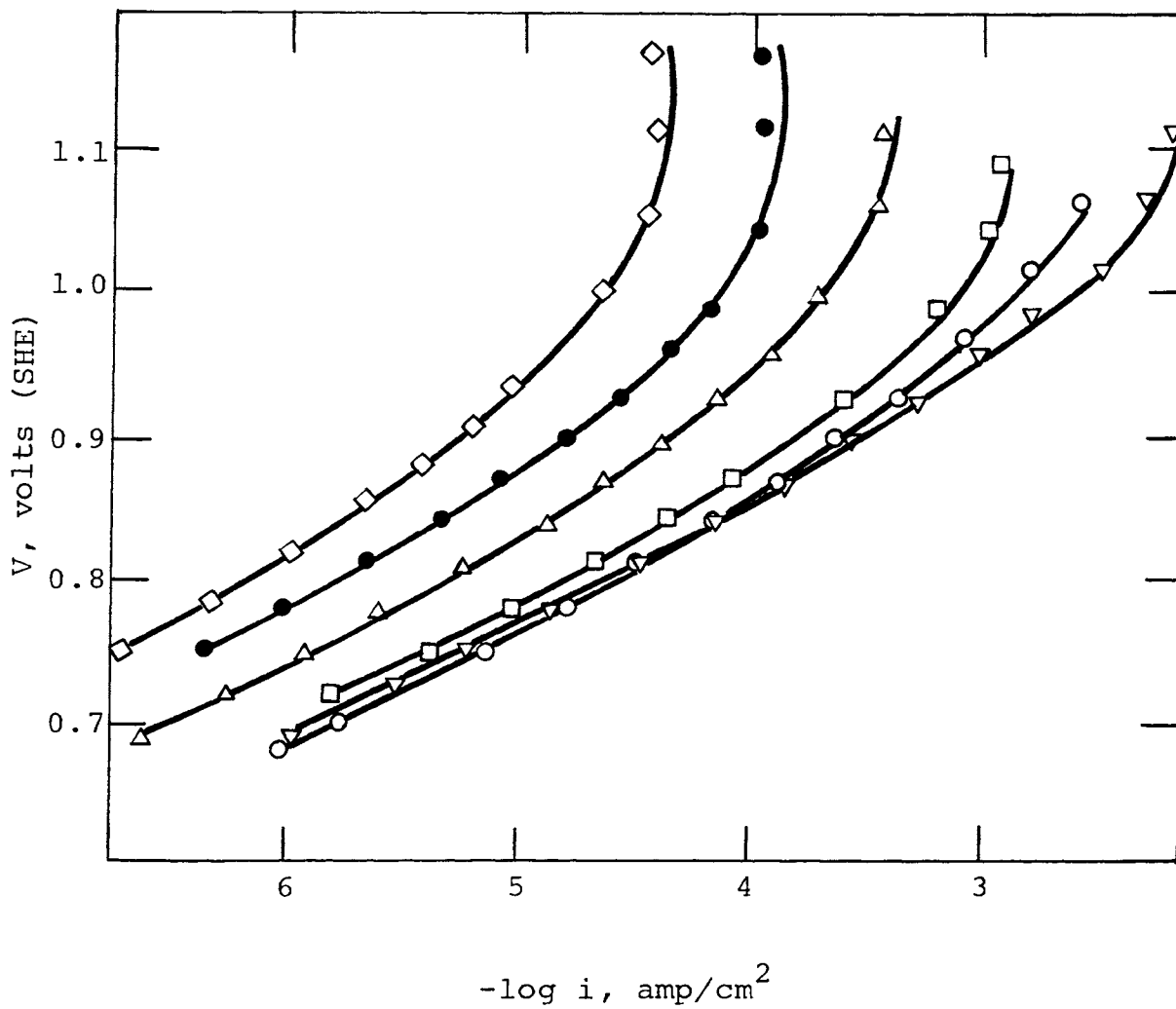


Figure 1.

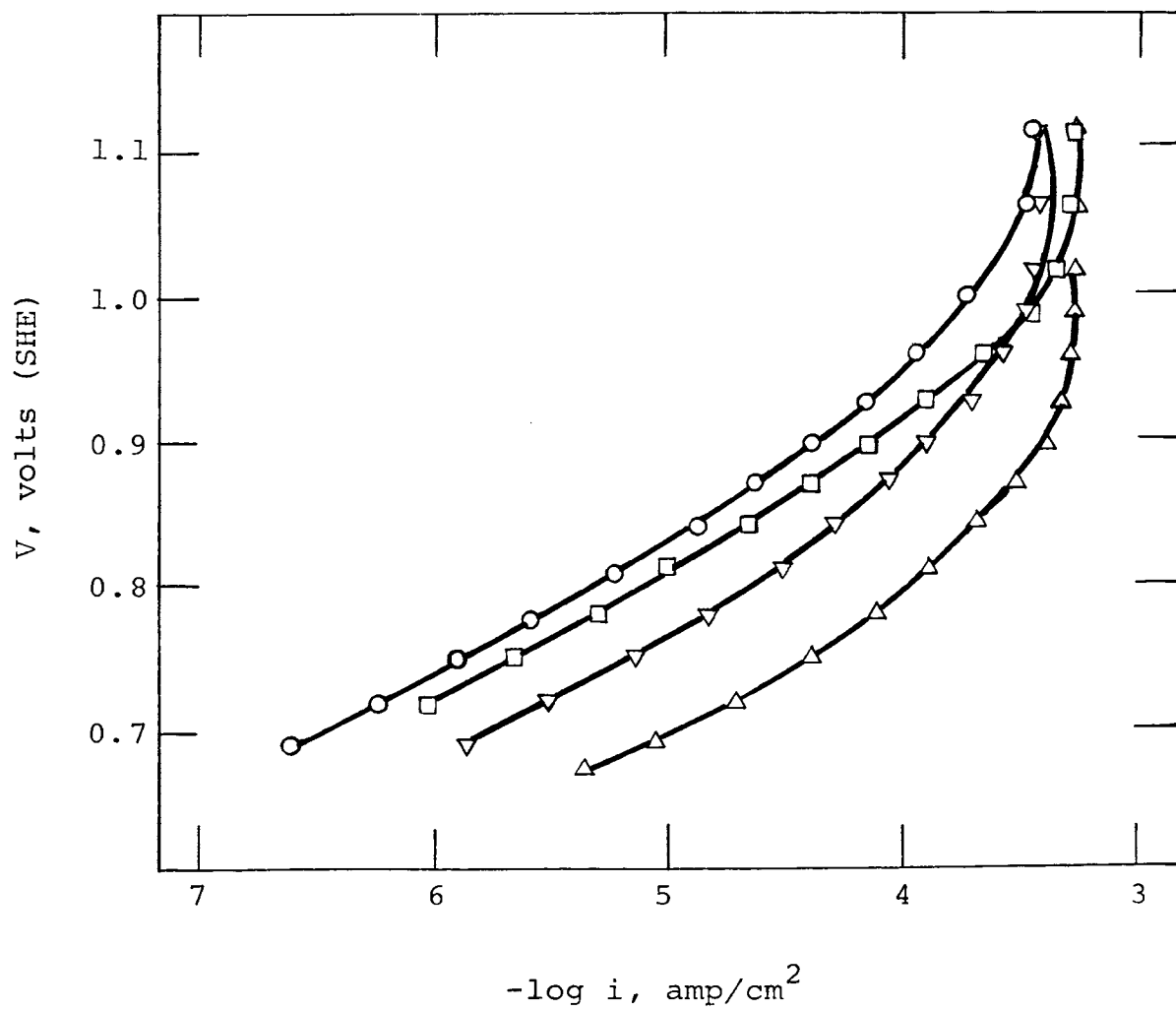


Figure 2.

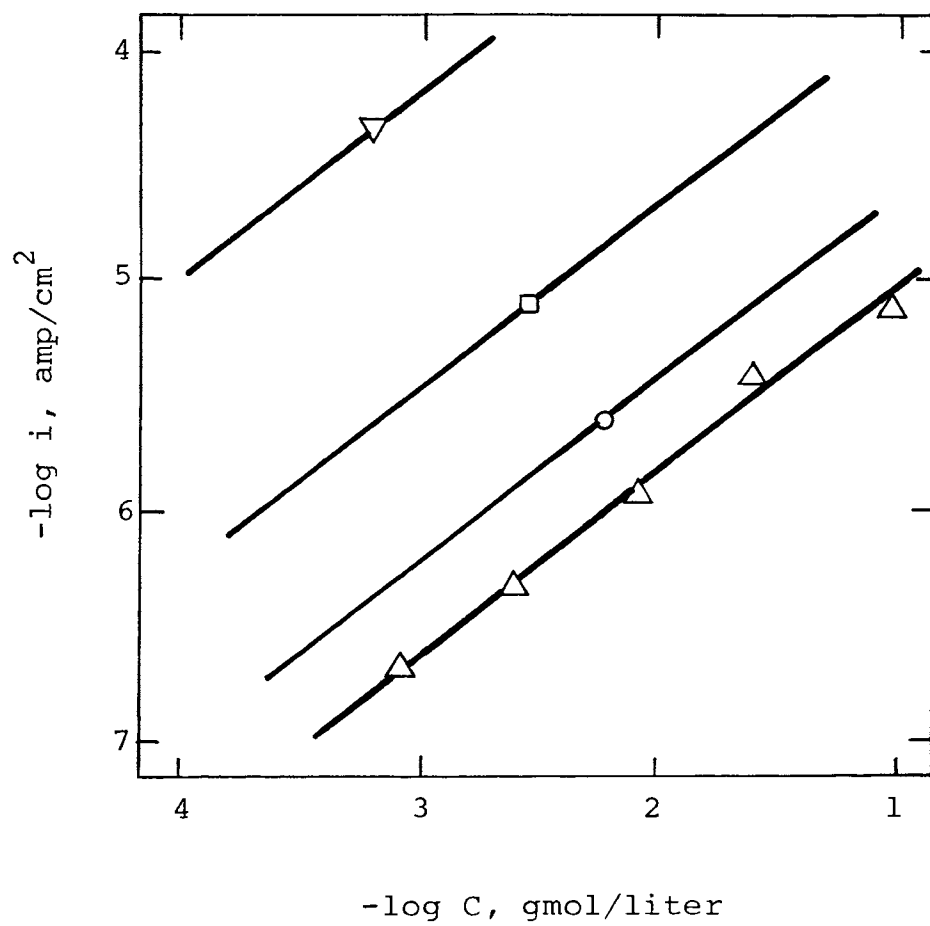


Figure 3.

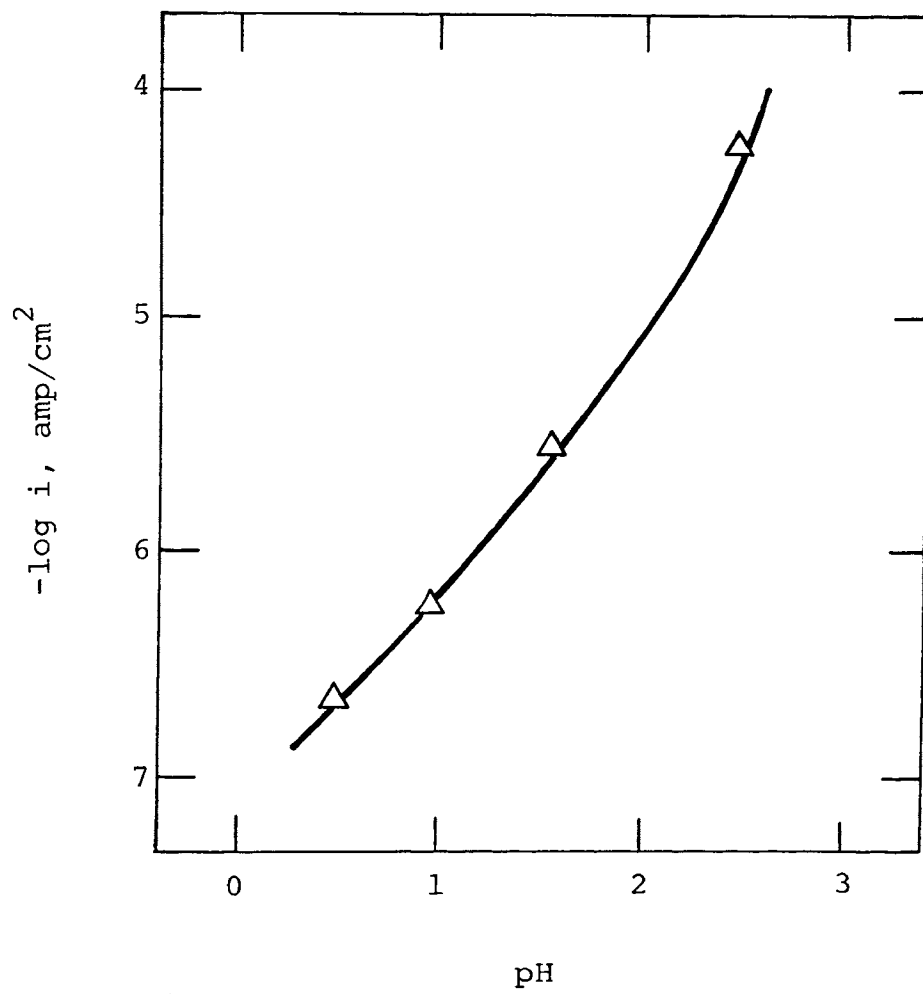


Figure 4.

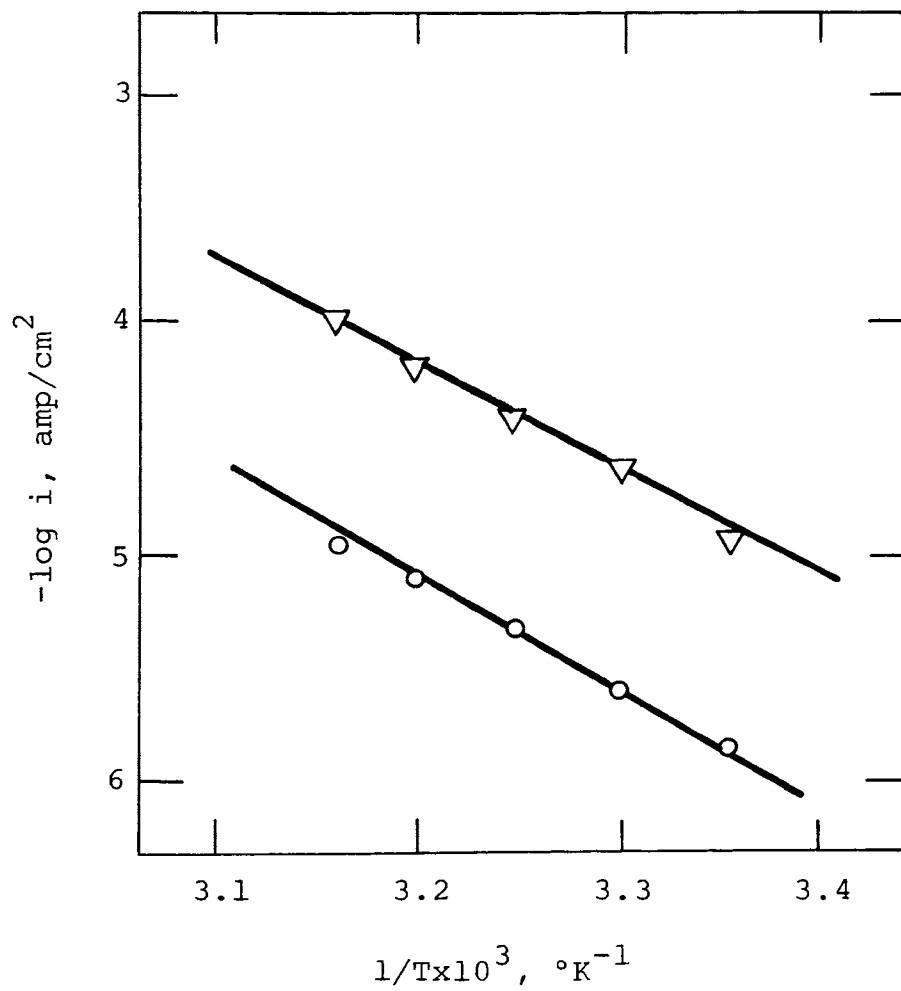


Figure 5.

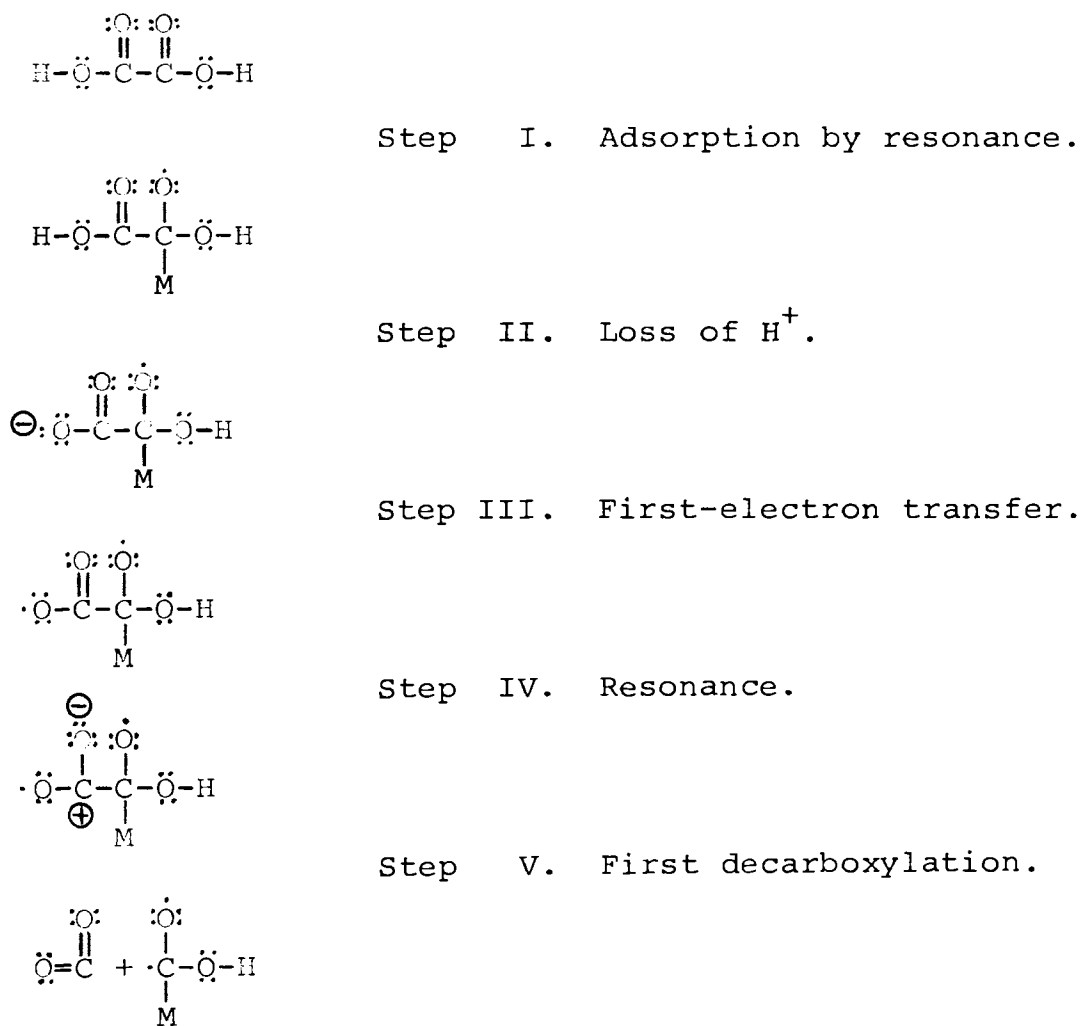


Figure 6.

APPENDIX A

MATERIALS

1. Oxalic Acid. Fisher Certified Reagent, Fisher Chemical Company, Fairlawn, N. J.
2. Potassium Sulfate. Fisher Certified Reagent, Fisher Chemical Company, Fairlawn, N. J.
3. Sulfuric Acid. Fisher Certified Reagent, Fisher Chemical Company, Fairlawn, N. J.
4. Ascarite. 20-30 Mesh Lot #8120, Arthur H. Thomas Company, Philadelphia, Pa.
5. Nitrogen. Matheson Pre-purified Grade, Matheson Company, Chicago, Ill.

APPENDIX B

APPARATUS

1. Potentiostat. Wenking No. 6356TR, Brinkman Instruments, Great Neck, N.Y.
2. Recorder. Esterline-Angus Graphis Ammeter, 0-1 ma, Esterline-Angus Company, Indianapolis, Indiana.
3. Power Resistor. Decade box Mod. No. 240-C, Clarostat Manufacturing Co., Dover, N. H.
4. Power Supply. Hewlitt-Packard Mod. 711A, 0-500 v.d.c., Hewlitt-Packard Co., Palo Alto, Calif.
5. Power Supply. Gates D.C. Power Supply, 0-500 v.d.c., Gates Electronics Co., New York, N. Y.
6. Electrometer. Keithly 610B, Keithly Instruments, Cleveland, Ohio.

APPENDIX C

DATA

TABLE II

CURRENT-POTENTIAL VALUES FOR THE ANODIC OXIDATION
 OF OXALIC ACID IN 1 N H₂SO₄ (T = 25°C)
 OXALIC ACID CONCENTRATION = 0.001 M

Potential*	Potential	Total Current	Current Density
V(NSE)	V(SHE)	ma	amp/cm ²
+0.080	+0.752	0.003	2.0x10 ⁻⁷
+0.110	+0.782	0.007	4.6x10 ⁻⁷
+0.150	+0.822	0.017	1.1x10 ⁻⁶
+0.180	+0.852	0.031	2.1x10 ⁻⁶
+0.210	+0.882	0.058	3.9x10 ⁻⁶
+0.240	+0.912	0.095	6.2x10 ⁻⁶
+0.270	+0.242	0.135	9.0x10 ⁻⁶
+0.300	+0.972	0.24	1.6x10 ⁻⁵
+0.330	+1.002	0.32	2.1x10 ⁻⁵
+0.360	+1.032	0.42	2.8x10 ⁻⁵
+0.390	+1.062	0.54	3.6x10 ⁻⁵
+0.420	+1.092	0.57	3.8x10 ⁻⁵
+0.450	+1.122	0.58	3.9x10 ⁻⁵
+0.500	+1.172	0.53	3.5x10 ⁻⁵

*Hg/Hg₂SO₄ (1 N H₂SO₄), V = +0.672 V(SHE)

TABLE III

CURRENT-POTENTIAL VALUES FOR THE ANODIC OXIDATION
 OF OXALIC ACID IN 1 N H₂SO₄ (T = 25°C)
 OXALIC ACID CONCENTRATION = 0.003 M

Potential*	Potential	Total Current	Current Density
V(NSE)	V(SHE)	ma	amp/cm ²
+0.080	+0.752	0.007	4.7x10 ⁻⁷
+0.110	+0.782	0.015	1.0x10 ⁻⁶
+0.140	+0.812	0.035	2.3x10 ⁻⁶
+0.170	+0.842	0.068	4.5x10 ⁻⁶
+0.200	+0.872	0.13	8.7x10 ⁻⁵
+0.230	+0.902	0.24	1.6x10 ⁻⁵
+0.260	+0.932	0.41	2.7x10 ⁻⁵
+0.290	+0.962	0.66	4.6x10 ⁻⁵
+0.320	+0.992	0.99	6.6x10 ⁻⁵
+0.350	+1.022	1.35	9.0x10 ⁻⁵
+0.380	+1.052	1.65	1.1x10 ⁻⁴
+0.410	+1.082	1.8	1.2x10 ⁻⁴
+0.450	+1.122	1.8	1.2x10 ⁻⁴
+0.500	+1.172	1.7	1.1x10 ⁻⁴

*Hg/Hg₂SO₄ (1 N H₂SO₄), V = +0.672 V(SHE)

TABLE IV

CURRENT-POTENTIAL VALUES FOR THE ANODIC OXIDATION
 OF OXALIC ACID IN 1 N H_2SO_4 (T = 25°C)
 OXALIC ACID CONCENTRATION = 0.01 M

Potential*	Potential	Total Current	Current Denisty
V(NSE)	V(SHE)	ma	amp/cm ²
+0.020	+0.692	0.004	2.7×10^{-7}
+0.050	+0.722	0.009	6.0×10^{-7}
+0.080	+0.752	0.019	1.3×10^{-6}
+0.110	+0.782	0.041	2.7×10^{-6}
+0.140	+0.812	0.086	5.7×10^{-6}
+0.170	+0.842	0.173	1.5×10^{-5}
+0.200	+0.872	0.34	2.3×10^{-5}
+0.230	+0.902	0.62	4.1×10^{-5}
+0.260	+0.932	1.10	7.3×10^{-5}
+0.290	+0.962	2.15	1.4×10^{-4}
+0.320	+0.992	2.9	1.9×10^{-4}
+0.350	+1.022	3.9	2.6×10^{-4}
+0.400	+1.072	5.1	3.4×10^{-4}
+0.450	+1.122	5.3	3.5×10^{-4}

*Hg/Hg₂ SO₄ (1 N H₂SO₄), V = +0.672 V(SHE)

TABLE V

CURRENT-POTENTIAL VALUES FOR THE ANODIC OXIDATION
 OF OXALIC ACID IN 1 N H₂SO₄ (T = 25°C)
 OXALIC ACID CONCENTRATION = 0.03 M

Potential*	Potential	Total Current	Current Denisty
V(NSE)	V(SHE)	ma	amp/cm ²
+0.050	+0.722	0.026	1.7x10 ⁻⁶
+0.080	+0.752	0.0625	4.2x10 ⁻⁶
+0.110	+0.782	0.145	9.7x10 ⁻⁶
+0.140	+0.812	0.31	2.1x10 ⁻⁵
+0.170	+0.842	0.65	4.3x10 ⁻⁵
+0.200	+0.872	1.27	8.5x10 ⁻⁵
+0.230	+0.902	2.3	1.5x10 ⁻⁴
+0.260	+0.932	3.95	2.6x10 ⁻⁴
+0.290	+0.962	6.3	4.2x10 ⁻⁴
+0.320	+0.992	9.5	6.3x10 ⁻⁴
+0.350	+1.022	14	9.4x10 ⁻⁴
+0.380	+1.052	17	1.1x10 ⁻³
+0.410	+1.082	18	1.2x10 ⁻³

*Hg/Hg₂SO₄ (1 N H₂SO₄), V = +0.672 V(SHE)

TABLE VI

CURRENT-POTENTIAL VALUES FOR THE ANODIC OXIDATION
 OF OXALIC ACID IN 1 N H₂SO₄ (T = 25°C)
 OXALIC ACID CONCENTRATION = 0.1 M

Potential*	Potential	Total Current	Current Density
V(NSE)	V(SHE)	ma	amp/cm ²
+0.010	+0.682	0.014	9.3x10 ⁻⁷
+0.030	+0.702	0.026	1.7x10 ⁻⁶
+0.050	+0.722	0.046	3.1x10 ⁻⁶
+0.080	+0.752	0.11	7.4x10 ⁻⁶
+0.110	+0.782	0.24	1.6x10 ⁻⁵
+0.140	+0.812	0.52	3.5x10 ⁻⁵
+0.170	+0.842	1.0	6.7x10 ⁻⁵
+0.200	+0.872	1.9	1.3x10 ⁻⁴
+0.230	+0.902	3.4	2.3x10 ⁻⁴
+0.260	+0.932	6.0	4.0x10 ⁻⁴
+0.300	+0.972	12.0	8.0x10 ⁻⁴
+0.350	+1.022	25	1.7x10 ⁻³
+0.400	+1.072	42	2.8x10 ⁻³

*Hg/Hg₂SO₄ (1 N H₂SO₄), V = +0.672 V(SHE)

TABLE VII

CURRENT-POTENTIAL VALUES FOR THE ANODIC OXIDATION
 OF OXALIC ACID IN 1 N H₂SO₄ (T = 25°C)
 OXALIC ACID CONCENTRATION = 0.3 M

Potential*	Potential	Total Current	Current Density
V(NSE)	V(SHE)	ma	amp/cm ²
+0.020	+0.692	0.017	1.1x10 ⁻⁶
+0.050	+0.722	0.037	2.5x10 ⁻⁶
+0.080	+0.752	0.102	6.8x10 ⁻⁶
+0.110	+0.782	0.23	1.5x10 ⁻⁵
+0.140	+0.812	0.50	3.3x10 ⁻⁵
+0.170	+0.842	1.0	6.7x10 ⁻⁵
+0.200	+0.872	2.0	1.3x10 ⁻⁴
+0.230	+0.902	4.1	2.7x10 ⁻⁴
+0.260	+0.932	8.3	5.5x10 ⁻⁴
+0.290	+0.962	14.2	9.5x10 ⁻⁴
+0.320	+0.992	24.5	1.6x10 ⁻³
+0.350	+1.022	38	2.5x10 ⁻³
+0.402	+1.072	70	4.7x10 ⁻³
+0.452	+1.122	112	7.5x10 ⁻³

*Hg/Hg₂SO₄ (1 N H₂SO₄), V = +0.672 V(SHE)

TABLE VIII

CURRENT-POTENTIAL VALUES FOR THE ANODIC OXIDATION
 OF OXALIC ACID IN 1 N $\text{H}_2\text{SO}_4/\text{K}_2\text{SO}_4$ ($T = 25^\circ\text{C}$)
 TOTAL OXALIC ACID CONCENTRATION = 0.01 M ($\text{pH} = 1.0$)

Potential*	Potential	Total Current	Current Density
V(NSE)	V(SHE)	ma	amp/cm ²
+0.050	+0.722	0.014	9.3×10^{-7}
+0.080	+0.752	0.033	2.2×10^{-6}
+0.110	+0.782	0.078	5.2×10^{-6}
+0.140	+0.812	0.155	1.0×10^{-5}
+0.170	+0.842	0.32	2.2×10^{-5}
+0.200	+0.872	0.63	4.2×10^{-5}
+0.230	+0.902	1.15	7.6×10^{-5}
+0.260	+0.932	2.08	1.4×10^{-4}
+0.290	+0.962	3.4	2.3×10^{-4}
+0.320	+0.992	5.1	3.4×10^{-4}
+0.350	+1.022	6.25	4.2×10^{-4}
+0.400	+1.072	7.7	5.1×10^{-4}
+0.450	+1.122	8.0	5.3×10^{-4}

* $\text{Hg}/\text{Hg}_2\text{SO}_4$ (1 N H_2SO_4), $V = +0.672$ V(SHE)

TABLE IX

CURRENT-POTENTIAL VALUES FOR THE ANODIC OXIDATION
 OF OXALIC ACID IN 1 N $\text{H}_2\text{SO}_4/\text{K}_2\text{SO}_4$ ($T = 25^\circ\text{C}$)
 TOTAL OXALIC ACID CONCENTRATION = 0.01 M (pH = 1.6)

Potential*	Potential	Total Current	Current Density
V(NSE)	V(SHE)	ma	amp/cm ²
+0.020	+0.692	0.022	1.5×10^{-6}
+0.050	+0.722	0.048	3.2×10^{-6}
+0.080	+0.752	0.11	7.4×10^{-6}
+0.110	+0.782	0.23	1.5×10^{-5}
+0.140	+0.812	0.46	3.1×10^{-5}
+0.170	+0.842	0.80	5.3×10^{-5}
+0.200	+0.872	1.35	9.2×10^{-4}
+0.230	+0.902	2.0	1.3×10^{-4}
+0.260	+0.932	3.0	2.0×10^{-4}
+0.290	+0.962	4.0	2.7×10^{-4}
+0.320	+0.992	4.9	3.3×10^{-4}
+0.350	+1.022	5.45	3.6×10^{-4}
+0.400	+1.072	5.3	3.5×10^{-4}
+0.450	+1.122	4.8	3.2×10^{-4}

* $\text{Hg}/\text{Hg}_2\text{SO}_4$ (1 N H_2SO_4), $V = +0.672$ V(SHE)

TABLE X

CURRENT-POTENTIAL VALUES FOR THE ANODIC OXIDATION
 OF OXALIC ACID IN 1 N $\text{H}_2\text{SO}_4/\text{K}_2\text{SO}_4$ ($T = 25^\circ\text{C}$)
 TOTAL OXALIC ACID CONCENTRATION = 0.01 M (pH = 2.4)

Potential*	Potential	Total Current	Current Density
V(NSE)	(VSHE)	ma	amp/cm ²
0.000	+0.672	0.070	4.7×10^{-6}
+0.020	+0.692	0.13	9.2×10^{-6}
+0.050	+0.722	0.30	2.0×10^{-5}
+0.080	+0.752	0.63	4.2×10^{-5}
+0.110	+0.782	1.2	8.0×10^{-5}
+0.140	+0.812	2.05	1.4×10^{-4}
+0.170	+0.842	3.2	2.1×10^{-4}
+0.200	+0.872	4.7	3.1×10^{-4}
+0.230	+0.902	6.1	4.1×10^{-4}
+0.260	+0.932	7.2	4.8×10^{-4}
+0.290	+0.962	8.0	5.3×10^{-4}
+0.320	+0.992	8.6	5.7×10^{-4}
+0.350	+1.022	8.7	5.8×10^{-4}
+0.400	+1.072	8.8	5.8×10^{-4}

* $\text{Hg}/\text{Hg}_2\text{SO}_4$ (1 N H_2SO_4), $V = +0.672$ V(SHE)

TABLE XI

CONCENTRATION AND pH EFFECTS FOR THE ANODIC OXIDATION
 OF OXALIC ACID IN 1 N $\text{H}_2\text{SO}_4/\text{K}_2\text{SO}_4$ (T = 25°C)
 AT CONSTANT POTENTIAL V = +0.752 V(SHE)*

Total Concentration	pH Measured	Unionized Oxalic Acid Concentration	Current	Current Density
gmol/liter		gmol/liter	ma	amp/cm ²
0.001	0.5	8.6×10^{-4}	0.003	2×10^{-7}
0.003	0.5	2.6×10^{-3}	0.007	4.7×10^{-7}
0.01	0.5	8.6×10^{-3}	0.019	1.2×10^{-6}
0.03	0.5	2.6×10^{-3}	0.062	4.1×10^{-6}
0.1	0.5	8.6×10^{-2}	0.11	7.3×10^{-6}
0.01	1.0	6.5×10^{-3}	0.038	2.5×10^{-6}
0.01	1.6	3.15×10^{-3}	0.11	7.4×10^{-6}
0.01	2.4	6.8×10^{-4}	0.68	4.5×10^{-5}

*Selected arbitrarily

TABLE XII

CURRENT-TEMPERATURE VALUES FOR THE ANODIC OXIDATION
 OF OXALIC ACID IN 1 N H₂SO₄
 OXALIC ACID CONCENTRATION = 0.1 M

Temperature	Potential*	Potential	Total Current	Current Density
0.1°C	V(NSE)	V(SHE)	ma	amp/cm ²
43.2	+0.030	+0.702	0.16	1.07x10 ⁻⁵
39.6	+0.030	+0.702	0.115	7.66x10 ⁻⁵
34.8	+0.030	+0.702	0.068	4.54x10 ⁻⁶
29.8	+0.030	+0.702	0.0375	2.5x10 ⁻⁶
24.8	+0.030	+0.702	0.022	1.47x10 ⁻⁶
43.6	+0.110	+0.782	1.50	1.0x10 ⁻⁴
39.6	+0.110	+0.782	1.0	6.66x10 ⁻⁵
34.8	+0.110	+0.782	0.56	3.73x10 ⁻⁵
29.8	+0.110	+0.782	0.35	2.33x10 ⁻⁵
24.8	+0.110	+0.782	0.173	1.16x10 ⁻⁵

*Hg/Hg₂SO₄ - 1 N H₂SO₄, V = +0.672 V(SHE)

VITA

Jean Louis Lucien Desmartin was born on August 18, 1945 in VANOSC (07), FRANCE. He received his primary and secondary education in Annonay, France. After two years of preparation in the "Lycee du Pare", LYON, FRANCE, he entered the Advanced School of Chemistry in Lyon, from which he graduated in the year 1969. He has been enrolled in the Graduate School of the University of Missouri-Rolla since September, 1969 and has held a research assistantship from the Graduate Center for Materials Research during the period September, 1969, to August, 1970.