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MILLER, Leo C., 1947-
KINETICS AND MECHANISM OF TWO REDOX REACTIONS: I. THE OXIDATION OF FORMIC ACID BY SILVER(II). II. THE OXIDATION OF OXALIC ACID BY SILVER(II).

The City University of New York
Ph.D., 1976
Chemistry, inorganic

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II. THE OXIDATION OF OXALIC ACID BY SILVER(II).

by

LEO C. MILLER

A dissertation submitted to the Graduate Faculty
in Chemistry in partial fulfillment of the
requirements for the degree of Doctor of
Philosophy, The City University of New York.

January
1976

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

1/20/76
date

Jack I. Morrow
Chairman of Examining Committee

1/20/76
date

Leonard H. Schwartz
Executive Officer

Irving Waltcher
Supervisory Committee

The City University of New York

ABSTRACT

KINETICS AND MECHANISM OF TWO REDOX REACTIONS:
I. THE OXIDATION OF FORMIC ACID BY SILVER(II),
II. THE OXIDATION OF OXALIC ACID BY SILVER(II).

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LEO C. MILLER

Mentor: Professor Jack I. Morrow

The kinetics and mechanism for the reaction of silver(II) with formic acid, a monocarboxylic acid, and oxalic acid, a dicarboxylic acid, have been investigated using the stopped-flow technique.

The study of the oxidation of formic acid by silver(II) in 0.71M to 6.3M nitric acid solutions results in a rate expression of the form,

$$-\tfrac{1}{2}\, d[Ag(II)]/dt = \frac{k[Ag(II)][HCO_2H]_T}{\{1+K[NO_3^-]\}[H^+]}$$

at 25 °C and constant ionic strength. Two possible reaction pathways resulting in the same rate expression, consistent with all the data, are discussed. The mechanisms differ in that one involves the formation of an intermediate complex ion and the other does not.

With regard to oxalic acid, its oxidation by silver(II) in 2.2M to 6.0M nitric acid solutions results in a rate expression of the form,

$$-\tfrac{1}{2}\, d[Ag(II)]/dt = \left\{\frac{k'}{[H^+]} + \frac{k''}{[H^+]^2}\right\}[Ag(II)][H_2C_2O_4]_T$$

at 5 °C and constant ionic strength.

The different forms of the rate expressions for the two reactions studied indicate significantly different mechanistic pathways are involved in these reactions. Particularly striking is the absence of a nitrate ion dependence for the oxalic acid-silver(II) reaction, while the formic acid-silver(II) reaction exhibits a definite nitrate ion inhibition. In both studies a free radical reaction pathway is indicated. Similarities and differences in the reactions are discussed.

to

my wife,

Sunny

and

my son,

Eric

ACKNOWLEDGMENTS

Many heartfelt thanks are due Professor Jack I. Morrow for his understanding and guidance that ensured the successful completion of this work.

I also wish to thank Professor Juan F. Villa (Thesis Committee Member) for his assistance with the e.s.r. experiments and for useful discussions.

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INTRODUCTION

A. Silver(II) Chemistry

As early as 1809 it was known that a black material was produced at a platinum anode during the electrolysis of silver(I) salts.[1] One hundred and twenty-six years later Noyes and coworkers[2] used magnetic susceptibility measurements to show that the black material dissolved in nitric acid solution was the paramagnetic silver(II) species. The electron spin resonance spectra of silver(II) in liquid and frozen acidic solutions have been examined by Mc Millan and Smaller.[3] The e.s.r. spectrum of silver(II) in nitric acid solution is a single broad line with a g value[4] of 2.133.

The silver(II) species in acidic[5,6,7,8] and alkaline[5,9,10] media has been extensively investigated by numerous researchers. In aqueous nitric acid media a 1 : 1 silver(II)-nitrate ion complex is formed.[11,12] Honig and Kustin[13] have found that the nitratosilver(II) equilibrium constant for the reaction

$$Ag^{2+} + NO_3^- \rightleftharpoons AgNO_3^+ \qquad (1)$$

is $0.94M^{-1}$ via spectrophotometric methods. Similarly, Ag^{2+} hydrolyzes in aqueous perchloric acid according to the reaction

$$Ag^{2+} + HOH \rightleftharpoons AgOH^+ + H^+ \ . \qquad (2)$$

The equilibrium constant is equal to $0.72M^{-1}$.[13] No evidence has been found to show that silver(II)-perchlorate complexation occurs in aqueous acid solution.[12,13,14] Studies[15,16,17] attempting to show this type of complexation have been interpreted on the basis of medium effects.[14] Others[18] have studied the stability of silver(II) in acidic sulphate media but only speculate on the existence of silver(II)-sulfate complexes.

Noyes and coworkers[2,12,19,20,21] among other[3,5,15,16,22] researchers have shown that silver(II) in mineral acid solutions will rapidly disproportionate to yield silver(I) and silver(III).

$$2Ag(II) \rightleftharpoons Ag(I) + Ag(III) \qquad (3)$$

This equilibrium lies far to the left. The silver(II) concentration is over 3.3×10^3 fold greater than the silver(III) concentration.[23] Additionally, Gordon and Wahl[24] have investigated the exchange reaction between silver(I) and silver(II) and have proposed that the reaction proceeds via the bimolecular reaction of silver(II) previously given.

Silver(II) ions have been generated in acid media either by dissolution of silver(II) oxide in mineral acid solution or by the anodic oxidation of silver(I) to silver(II) in mineral acid solution. The preparation of silver(II) oxide has been reported by many workers.[25] One method used to prepare silver(II) oxide involves the oxidation of silver(I) in solution by alkaline peroxodisulfate.[26,27,28,29] Numerous researchers[12,18,21,30,31,32] have used electrolytic methods to generate silver(II) from silver(I) salts (e.g. nitrate, perchlorate and sulfate) in the appropriate mineral acid solution. Another preparative method used to generate silver(II) is the oxidation of silver(I) in nitric acid solution by ozone.[15,20,33]

Diamagnetic silver(II) oxide has been shown to be Ag(I)Ag(III)O_2 in the crystalline state by neutron diffraction.[5,34,35,36] However, silver(II) oxide has been shown to dissolve in nitric acid, perchloric acid and to a lesser extent sulfuric acid to yield silver(II) ions.[2,7,37] Silver(II) oxide was used in this study.

Silver(II) has been used in quantitative analysis as an oxidimetric reagent for trace metal analysis. Kimura and Murakami[28] and Tanaka[38] have reported that silver(II) may be used in microanalysis involving manganese determinations in biological materials, silicate rocks and natural waters. These researchers conclude that using silver(II) for manganese analyses overcomes many of the difficulties previously encountered using sodium bismuthate and ammonium peroxodisulfate. Ligane and Davis[39] studied the use of silver(II) as an oxidimetric reagent for determinations of manganese(II), cerium(III) and chromium(III). These workers observed that when silver(II) oxide is dissolved in cold nitric acid, perchloric acid or sulfuric acid solutions of Mn(II), Ce(III) or Cr(III) oxidation to MnO_4^-, Ce(IV) or $Cr_2O_7^{2-}$ occurs rapidly. The resultant solutions of permanganate, cerium(IV) or dichromate are then titrated with standardized iron(II) solutions photometrically or potentiometrically.

Reaction kinetics involving silver(II) has been found of interest by numerous investigators. Firstly, silver(II) is an exceptionally powerful oxidizing agent in mineral acid solutions. The Ag(II)/Ag(I) couple is +1.93V in 4M nitric acid[40] and$+1.97$V in 4M perchloric acid[12] at 25°C making silver(II) one of the strongest one electron oxidants.[41] Aside from its exceptionally high oxidation potential, kinetically its reactions are usually rapid. The reaction of silver(II) with hydrogen peroxide,[23,42] hydroquinone,[42] nitrous ion,[42] and hydrazine[43] is essentially complete within the resolution time of the stopped-flow apparatus(~2 msec). Previous studies of redox reactions involving silver(II) have shown an interesting variety of mechanistic behavior. There are generally two ways in which silver(II) can function as an oxidant.

I $\quad \mathrm{Ag(II)} + \mathrm{S} \longrightarrow \mathrm{Ag(I)} + \mathrm{S}^{+}$

II $\quad 2\mathrm{Ag(II)} \rightleftharpoons \mathrm{Ag(I)} + \mathrm{Ag(III)}$

$\quad \mathrm{Ag(III)} + \mathrm{S} \longrightarrow \mathrm{Ag(I)} + \mathrm{S}^{2+}$

S represents any oxidizable substrate. If S^{+} and S^{2+} are not the final products then they will participate in subsequent reactions leading to final reaction products. Substrates that react via scheme I with silver(II) are Fe(II), Co(II),[44] Ce(III),[39,44] Mn(II),[44,45] $\mathrm{Hg_2(II)}$,[46] Tl(I),[46,47] V(IV),[44,48,49,50] Cr(III),[45,51] $\mathrm{NH_3}$,[10] $\mathrm{NH_2OH}$[42] and $(\mathrm{S_2O_6}^{2-})$.[31] In additon to the studies involving the reaction of silver(II) with the above species its reaction with aqueous phosphorous acid,[52] nitric acid,[19,20,23] perchloric acid,[15,16,53] sulfuric acid,[18] and phosphoric acid[54] solutions indicate that the predominant reaction pathway for these substrates is by way of scheme II or by a combination of reaction schemes I and II. Noyes *et al.*[19,20] found the stoichiometry for the slow oxidation of water in the presence of silver(II) in nitric acid solution to be

$$4Ag(II) + 2H_2O \longrightarrow 4Ag(I) + 4H^+ + O_2 \;. \qquad (4)$$

It is interesting that for this reaction, where $[Ag(II)] \geq 1 \times 10^{-4}M$, the rate law has the form rate = $k_{OBSD}[Ag(II)]^2$. (The term k_{OBSD} is the observed pseudo-order rate constant.) Where $[Ag(II)] < 1 \times 10^{-4}M$ the rate law has the form rate = $k'_{OBSD}[Ag(II)]$ in the range of 2.0M to 6.2M nitric acid. This is an example of a substrate being oxidized through a combination of reaction pathways I and II.

To date only one reaction involving the silver(II) oxidation of any organic substrate has been reported. Kustin and coworkers[42] have reported the oxidation of O-methylhydroxylamine, NH_2OCH_3, and N-methylhydroxylamine, CH_3NHOH, in aqueous perchloric acid media. The mechanism for the oxidation of protonated O-methylhydroxylamine involved the following elementary steps.

$$Ag^{2+} + NH_3OCH_3^+ \longrightarrow Ag^+ + \cdot NHOCH_3 + 2H^+ \qquad k_5 \qquad (5)$$

$$AgOH^+ + NH_3OCH_3^+ \longrightarrow Ag^+ + \cdot NHOCH_3 + H_3O^+ \qquad k_6 \qquad (6)$$

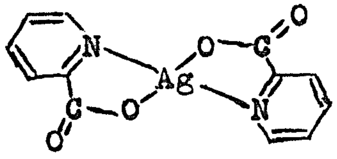
$$Ag(II) + \cdot NHOCH_3 \longrightarrow Ag^+ + \text{Products} \qquad k_7 \qquad (7)$$

It was found that $k_7 \gg k_5$ where steps 5, 6, and 7 represent one electron transfer processes. The rate determining steps are 5 and 6, which involve the formation of the free radical intermediates. These researchers compared the oxidation of the aforementioned species by silver(II) and manganese(III). They found that the O-methylhydroxylamine-silver(II) reaction is considerably faster than the O-methylhydroxylamine-manganese(III) reaction.[55] A table is presented to compare the values of the rate constants for the oxidation of a series of substrates by these oxidizing agents.

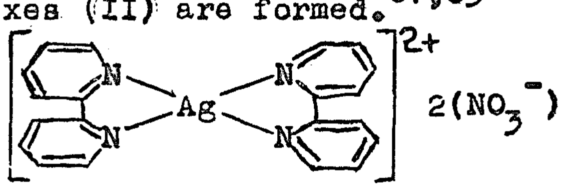
Substrate	Reactive Species (oxidants)			
	Ag^{2+}	$AgOH^{+}$	Mn^{3+}	$MnOH^{2+}$
NH_3OH^{+}	$<10^{4} M^{-1} sec^{-1}$	$1.4 x 10^{6} M^{-1} sec^{-1}$	$1.4 x 10^{3} M^{-1} sec^{-1}$	$3.1 x 10^{3} M^{-1} sec^{-1}$
$NH_3OCH_3^{+}$	$<10^{3} M^{-1} sec^{-1}$	$2.0 x 10^{4} M^{-1} sec^{-1}$	$< 0.5 M^{-1} sec^{-1}$	$6.1 M^{-1} sec^{-1}$

Apparently the $AgOH^{+}$ and $MnOH^{2+}$ are significantly more reactive than Ag^{2+} and Mn^{3+}, respectively. Since the redox couple Mn(III)/Mn(II) is +1.5V[56,57] this demonstrates that a substance with a higher oxidation potential may react more rapidly with a given substrate, although this is not always the case.

Comparatively few stable compounds of silver(II) have been synthesized and silver(II) fluoride is the only true binary compound of silver(II) known. Bis-(dipyridyl) silver(II) nitrate, $[Ag(dipyr)_2](NO_3)_2$, $[Ag(pyridine)_4](NO_3)_2$ and $[Ag(pyridine)_4]S_2O_8$ have been prepared by G.A. Barbieri.[58] This Italian chemist maintained leadership in the preparation of coordination compounds of silver(II) for about four decades beginning in 1906. Silver(II) has been found to coordinate with 8-hydroxyquinoline[59] as well as O-phenanthroline(O-phen) to form the peroxodisulfate complex, $[Ag(O\text{-}phen)_2]S_2O_8$, the hydrogen sulfate complex, $[Ag(O\text{-}phen)_2](HSO_4)_2$, plus the corresponding chlorate, perchlorate and nitrate complexes.[60] $[Ag(dipyr)_2](O_3SCF_3)_2$ has been recently prepared by the electrolysis of $Ag(I)(dipyr)_2(O_3SCF_3)$ in aqueous trifluoromethanesulfonic acid.[61] A series of silver(II) complexes of pyridine dicarboxylic acids have been prepared by Banarjee and Ray[62] which included nicotinate, isonicotinate, quinolinic, cinchomeronic, isocinchomeronic, lutidinic and dipicolinic acids as coordinating ligands. Walton and coworkers[63] have synthesized various complexes with a variety of mono- and dicarboxylic acids and have examined their magnetic and spectral properties. Murtha and Walton[64] have investigated the X-Ray Photoelectron Spectra of silver(II) complexes containing nitrogen donor molecules. Typically, silver(II) forms neutral complexes (I) with uninegative chelating ligands, such as 2-pyridine carboxylate, and with neutral ligands dipositive complexes (II) are formed.[61,65]



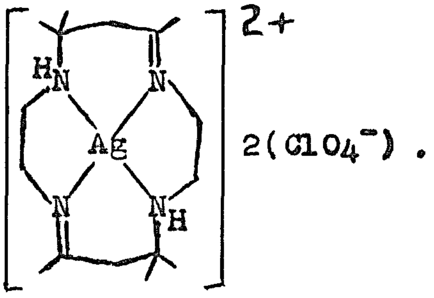
I



II

The complexes of silver(II) are usually prepared by the oxidation of silver(I) in the presence of the coordinating ligands (e.g. pyridine, orthophenanthroline, dipyridyl etc.). Barefield and Mocella[66] have shown that silver(I) can disproportionate in the presence of various ligands as follows $2Ag^+ + L \longrightarrow AgL^{2+} + Ag^0$. This general reaction occurred when silver(I) salts reacted with a variety of macrocyclic amines.[67] Utilizing this general reaction they were able to prepare silver(II) complexes with four macrocyclic tetraaza ligands. The general structure for the complex was given as follows.

III



Apparently the silver(II) species is stabilized by coordination to donor molecules, particularly nitrogen containing heterocycles such as bis and tris α, α′ bipyridyl and 1,10 phenanthroline.[68] This is attributed to the lowering of the Ag(II)/Ag(I) couple brought about by coordination, i.e. in the case of the dipyridyl from ~1.9V to 1.45V.[8,21,69]

The predominant geometry of all the silver(II) complexes is square planar and these are isomorphous with planar copper (II) analogs. Most of these silver(II) complexes have effective magnetic moments in the range of 1.75 to 2.2 Bohr magnetons consistent with the d^9 electronic configuration.[70] Two exceptions to the square planar geometry is 2,3- and 2,6-pyridine dicarboxylates and $Ag(C_7H_4NO_4)_2H_2O$ which have a distorted octahedral geometry.[71]

B. Formic Acid Reactions

The oxidation of formic acid by various inorganic oxidants has been investigated. Among the oxidants were Hg_2(II), Hg(II),[72,73] Tl(III),[72,74] Co(III),[75,76] Mn(III),[77,78,79] V(V),[76,80] Ce(IV),[81,82] Cr(VI),[76,83,84] Np(VII),[85] (MnO_4^-),[72,86-90] Pb(IV),[91] H_2O_2,[92] HIO_3,[93] Cl_2,[94] Br_2,[95] I_2,[96] O_3,[97] and ($S_2O_8^{2-}$).[98] In some of these studies it has been observed that the oxidation of formic acid can occur either through two successive one-electron transfer steps[72,73,75,76,79,80-83,98] or alternately through a two-electron transfer step.[74,78,87,88,90,96] In some of these reactions there was evidence that a complex ion intermediate was formed.[74,76,78,80-83]

A survey[72-75,77,79,81,83,88] of studies indicates that the stoichiometry for the oxidation of formic acid by an inorganic oxidant is $2M^{n+} + HCO_2H \longrightarrow 2M^{(n+)-1} + CO_2 + 2H^+$, where M^{n+} represents the oxidant.

Halpern and Taylor[72] studied the reaction of formic acid with mercury(I) and mercury(II) in perchloric acid media while Topham and White[73] studied the same reaction in nitric acid media. The elementary steps were found to be the same regardless of the media. The proposed rate determining steps are

$$Hg^{2+} + HCO_2H \longrightarrow Hg^{+} + HCO_2\cdot + H^{+} \tag{8}$$

$$Hg_2^{2+} + HCO_2H \longrightarrow Hg_2^{+} + HCO_2\cdot + H^{+} \tag{9}$$

$$Hg^{2+} + HCO_2^{-} \longrightarrow Hg^{+} + HCO_2\cdot \tag{10}$$

$$Hg_2^{2+} + HCO_2^{-} \longrightarrow Hg_2^{+} + HCO_2\cdot \tag{11}$$

$$HgOH^{+} + HCO_2^{-} \longrightarrow HgOH + HCO_2\cdot \tag{12}$$

$$Hg_2OH^{+} + HCO_2^{-} \longrightarrow Hg_2OH + HCO_2\cdot \; . \tag{13}$$

Both groups of workers postulated that the formyl free radical was formed in this reaction system. The formyl free radical reacts further to produce carbon dioxide. The fate of the mercury intermediates was not discussed by these researchers.

In a study of the oxidation of formic acid by thallium(III) the following mechanism was proposed by Halvorson and Halpern:[74]

$$Tl^{3+} + HCO_2H \rightleftharpoons TlHCO_2H^{3+} \tag{14}$$

$$TlHCO_2H^{3+} \longrightarrow Tl^{+} + CO_2 + 2H^{+} \; . \tag{15}$$

The mechanistic scheme includes the formation of a complex ion intermediate which is lost via a two-electron transfer (i.e. step 15). This is one of the few reactions in which the formyl free radical is not proposed.

Bawn and White[75] have investigated the oxidation of formic acid by cobalt(III) in 1M to 4M sulfuric acid solution. The rate determining steps were found to be

$$Co^{3+} + HCO_2H \longrightarrow Co^{2+} + HCO_2\cdot + H^+ \qquad (16)$$

$$Co^{3+} + HCO_2^- \longrightarrow Co^{2+} + HCO_2\cdot \; . \qquad (17)$$

In this study there was no evidence to indicate complex ion formation.

Beg and Ahmad[79] have studied the oxidation of formic acid by manganese(III) in 4M sulfuric acid medium, while Wells and Whatley[77] have studied the same reaction in 0.5M to 2.5M perchloric acid solutions. The mechanisms proposed in these studies were significantly different. In sulfuric acid medium the rate determining steps were

$$Mn^{3+} + HCO_2H \longrightarrow Mn^{2+} + CO_2\cdot + H^+ \qquad (18)$$

$$Mn^{3+} + HCO_2^- \longrightarrow Mn^{2+} + HCO_2\cdot \; . \qquad (19)$$

The formyl free radicals formed subsequently react with manganese(III) to form the reaction products. In perchloric acid solution the elementary steps were

$$Mn^{3+} + HCO_2H \rightleftharpoons MnHCO_2^{2+} + H^+ \qquad (20)$$

$$Mn^{3+} + HCO_2H \rightleftharpoons MnHCO_2H^{3+} \qquad (21)$$

$$MnHCO_2^{2+} \longrightarrow Mn^{2+} + HCO_2\cdot \qquad (22)$$

$$MnHCO_2H^{3+} \longrightarrow Mn^{2+} + HCO_2\cdot + H^+ \qquad (23)$$

$$Mn^{3+} + HCO_2\cdot \longrightarrow Mn^{2+} + CO_2 + H^+ \; . \qquad (24)$$

A comparison of these mechanisms indicate that the reaction pathway for the oxidation of formic acid is dependent on the counter ion.

In the case of the oxidation of formic acid by vanadium(V) [80] there is evidence for the formation of a complex ion intermediate, $HCO_2V(OH)_3^+$. It is postulated that this intermediate decomposes via a one-electron transfer step to form a carboxyl free radical ion ($CO_2^{\cdot -}$) which then reacts with vanadium(V) to yield carbon dioxide and vanadium(IV). This reaction pathway has been indicated in other studies.[74,77]

The kinetics and mechanism of the oxidation of formic acid by the aquocerium(IV) ion in aqueous perchlorate media has been investigated by Wells and Husain.[81] A fourteen step mechanism was proposed for this reaction. The major points of this complex mechanism were a). complex ion intermediates were formed (i.e. $CeHCO_2H^{4+}$, $CeHCO_2{}^{3+}$, and $CeHCO_2H_2{}^{5+}$ were postulated intermediates), b). the rate determining steps involved the decomposition of the complex ion intermediates, via one-electron transfer steps, to form free radical species and c). the subsequent reaction of the aquocerium(IV) ion with the free radical species to form carbon dioxide and cerium(III). Vasudevan and Mathai [82] have also studied the oxidation of formic acid by aquocerium(IV) in perchloric acid media. In 0.2M to 2.0M perchloric acid these workers proposed the following elementary steps:

$$Ce(H_2O)_8{}^{4+} + HCO_2H \rightleftharpoons [Ce(H_2O)_7HCO_2H]^{4+} + H_2O \qquad (25)$$

$$[Ce(H_2O)_7HCO_2H]^{4+} \longrightarrow [(H_2O)_7CeHCO_2]^{3+} + H^+ \qquad (26)$$

$$[(H_2O)_7CeHCO_2]^{3+} \longrightarrow Ce(H_2O)_6^{3+} + HCO_2\cdot + H_2O \qquad (27)$$

$$HCO_2^{\circ} \longrightarrow H^{\circ} + CO_2 \qquad (28)$$

$$H^{\circ} + H^{\circ} \longrightarrow H_2 \qquad (29)$$

$$H^{\circ} + Ce(H_2O)_8^{4+} \longrightarrow Ce(H_2O)_6^{3+} + H^+ + 2H_2O\ . \qquad (30)$$

This is the only reported case in which hydrogen gas is indicated as a reaction product. Significantly, these researchers claim that steps 28,29 and 30 were important although it would seem that the hydrogen atom concentration would be too low to allow step 29 to occur to any measurable extent.

The oxidation of formic acid by chromic acid has been postulated to occur via the reaction of protonated chromic acid, $O{=}CrO_3H_3^+$, with formic acid to yield the reaction products without any complex ion formation.[99] Alternatively, Venkatraman and Rao[83] and others[84] speculate that an intermediate complex , $H{-}\overset{+}{C}(OH){-}O{-}CrO_2{-}OH$, is first formed in the reaction between formic acid and chromic acid. This intermediate then undergoes slow decomposition to form carbon dioxide and chromium(IV).

Thompson and Sullivan[85] have studied the oxidation of formic acid by the very strong oxidant neptunium(VII). These workers were not able to distinguish between a reaction scheme involving successive one-equivalent steps or a sequence such as

$$Np(VII) + HCO_2H \longrightarrow Np(V) + CO_2 + 2H^+ \qquad (31)$$

$$Np(VII) + Np(V) \longrightarrow 2Np(VI) \text{ (rapid).} \qquad (32)$$

However, no complex ion intermediate formation was postulated to occur in this reaction. It is also interesting that a free radical species is not indicated as an intermediate in this system.

The oxidation of formic acid by the permanganate ion has been extensively studied by numerous workers.[100] Unfortunately, there remain many ambiguities in the mechanistic pathway of this oxidant with formic acid. The most commonly proposed reaction pathway involves the transfer of a hydride ion from the formate ion to the permanganate ion,

$$MnO_4^- + HCO_2^- \longrightarrow HMnO_4^{2-} + CO_2 \, . \tag{33}$$

Alternatively, it has been proposed that the first step involves the transfer of two electrons with the simultaneous transfer of a proton to the solvent, i.e.

$$MnO_4^- + HCO_2^- + H_2O \longrightarrow MnO_4^{3-} + CO_2 + H_3O^+ \, . \tag{34}$$

A hydrogen atom abstraction reaction reaction pathway is also plausible,

$$MnO_4^- + HCO_2^- \longrightarrow HMnO_4^- + CO_2^{\bullet -} \, . \tag{35}$$

This step may be followed by

$$MnO_4^- + CO_2^{\bullet -} \rightleftharpoons [O_2COMnO_3]^{2-} \tag{36}$$

$$[O_2COMnO_3]^{2-} \longrightarrow MnO_4^{2-} + CO_2 \, . \tag{37}$$

The loss of the complex ion intermediate, $[O_2COMnO_3]^{2-}$, is rate determining. The reaction of unionized formic acid and the permanganate ion in 4M sulfuric acid media[101] appears to follow a pathway involving permanganic acid as a reactive intermediate.

$$MnO_4^- + H^+ \rightleftharpoons HMnO_4 \tag{38}$$

$$HMnO_4 + HCO_2H \longrightarrow HMnO_3 + CO_2 + H_2O \tag{39}$$

$$3Mn(V) \rightleftharpoons 2Mn(IV) + Mn(VII) \tag{40}$$

In >9M sulfuric acid solution the reaction rate is significantly enhanced. This effect could be due to the formation of the permanganyl ion, MnO_3^+.[102]

The reaction between formic acid and lead tetraacetate[91] is unique since all other monocarboxylic acids are kinetically stable towards lead(IV) salts. Formic acid is readily and quantitatively converted to carbon dioxide at room temperature while all other monocarboxylic acids are oxidized only at elevated temperatures (i.e. ~100° C).

The reaction between the formate ion and the peroxodisulfate ion in aqueous acid solution has been investigated by Kimura.[98] The stoichiometry was found to be

$$S_2O_8^{2-} + HCO_2^- \longrightarrow 2SO_4^{2-} + H^+ + CO_2 \;. \qquad (41)$$

It was found that in three ranges of formate ion concentration the rate law has three essentially different forms. It is a complex reaction system. The proposed mechanism is a chain reaction involving $SO_4^{\cdot -}$, $OH^{\cdot}$, and $CO_2^{\cdot -}$ free radical species.

C. Oxalic Acid Reactions

The oxidation of oxalic acid has not been as extensively or intensively investigated with as many oxidants as with formic acid. The oxidizing agents used included Co(III),[103,104] Mn(III),[105] V(V),[107,108] Ce(IV),[109,110,111] Cr(VI),[108,112-116] (MnO_4^-),[117,118] ($S_2O_8^{2-}$),[119-121] Pb(IV),[106] and H_4XeO_6(Xenic Acid).[122] The preponderance of mechanisms for the oxidation of oxalic acid indicate that complex ion intermediates are formed before the actual electron transfer process takes place. Undoubtly, the apparent need for intermediate ion formation in the oxidation of oxalic acid can be ascribed to its ability to act as a uni- and/or bidentate ligand. It is noteworthy that in one study, to be discussed, a one-step three electron transfer mechanism was proposed.[115] It is also significant to note that while a number of stable metal ion-dicarboxylic acid complexes are known in aqueous solution,[123] there are no examples of silver(II)-dicarboxylic acid complexes stable in solution.

Sthapack and Ghosh[103] have investigated the reaction of cobalt(III) with oxalic acid. The mechanism that was presented involved the following steps.

$$[Co(H_2O)_5OH]^{2+} + H_2C_2O_4 \rightleftharpoons [Co(H_2O)_4(H_2C_2O_4)OH]^{2+} \qquad (42)$$

$$[Co(H_2O)_4(H_2C_2O_4)OH]^{2+} \longrightarrow Co^{2+} + HC_2O_4^{\circ} + H_2O \qquad (43)$$

$$Co^{3+} + HC_2O_4^{\circ} \longrightarrow Co^{2+} + 2CO_2 + H^+ \qquad (44)$$

The decomposition of bis- and tris- oxaltocobalt(III) complexes have been investigated.[104] Complex ion intermediates have been proposed in the mechanism. These intermediates subsequently react to form carbon dioxide and the carboxyl radical ion species. This free radical reacts further to produce another molecule of carbon dioxide. Some researchers[124] have postulated that ion pairing is important in the reactions involving cobalt(III) and chromium(III) complexes. In a study[125] of the complexation of oxalate to pentammineaquochromium(III) the following reactions were found to be of importance:

$$[Cr(NH_3)_5H_2O]^{3+} + HC_2O_4^- \rightleftharpoons [Cr(NH_3)_5H_2O]^{3+}, HC_2O_4^- \qquad (45)$$

$$[Cr(NH_3)_5H_2O]^{3+} + C_2O_4^{2-} \rightleftharpoons [Cr(NH_3)_5H_2O]^{3+}, C_2O_4^{2-} \qquad (46)$$

Taube[126] has proposed that complexes of the type

$Mn(C_2O_4)^+$ were formed in the reaction of oxalic acid with manganese(III). It was proposed in a study[127] of the chlorine oxidation of oxalic acid, catalyzed by manganese(II), that the following steps were significant.

$$Mn^{3+} + H_2C_2O_4 \rightleftharpoons MnC_2O_4{}^+ + 2H^+ \tag{47}$$

$$MnC_2O_4{}^+ + H_2C_2O_4 \rightleftharpoons Mn(C_2O_4)_2^- + 2H^+ \tag{48}$$

$$MnC_2O_4{}^+ \longrightarrow Mn^{2+} + C_2O_4{}^{\bullet -} \tag{49}$$

$$Cl_2 + C_2O_4{}^{\bullet -} \longrightarrow Cl + Cl^- + 2CO_2 \tag{50}$$

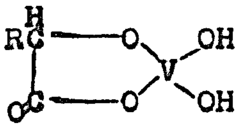
$$Mn^{2+} + Cl \longrightarrow Mn^{3+} + Cl^- \tag{51}$$

The slow step is 49 and steps 50 and 51 are needed for the regeneration of the reactive species.

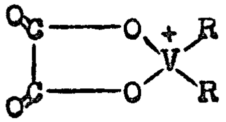
The oxidation of oxalic acid by vanadium(V) proceeds stoichiometrically according to

$$2V(V) + H_2C_2O_4 \longrightarrow 2V(IV) + 2CO_2 + 2H^+ \text{ .} \tag{52}$$

Jones and Waters[107] have proposed that complexes of the following type were involved as reactive intermediates:



IV



V

Others[108] have investigated this reaction and have shown that the following steps were important.

$$VO_2{}^+ + 2H_2C_2O_4 \rightleftharpoons VOH(C_2O_4)_2 + H_3O^+ \tag{53}$$

$$VOH(C_2O_4)_2 \longrightarrow VOH(C_2O_4)^+ + C_2O_4{}^{\bullet -} \tag{54}$$

The free radical ion species, $C_2O_4{}^{\bullet -}$, reacts with a vanadium(V) species to form the reaction products.

Furman[109] and Willard and Young[110] have established the stoichiometry for the oxidation of oxalic acid by cerium(IV) as follows,

$$2H_2Ce(ClO_4)_6 + H_2C_2O_4 \longrightarrow 2Ce(ClO_4)_3 + 6HClO_4 + 2CO_2. \quad (55)$$

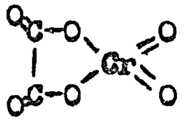
For the reaction of oxalic acid with cerium(IV) no intermediate complexation was reported.[111]

Bakore and Jain[112] have established the stoichiometry for the reaction between oxalic acid and chromium(VI) to be

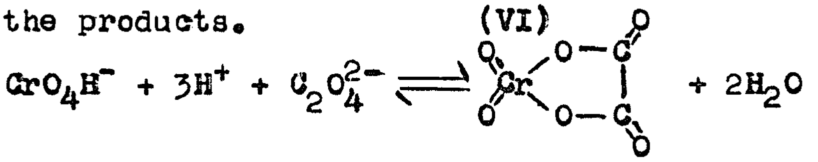
$$2Cr(VI) + 3H_2C_2O_4 \longrightarrow 2Cr(III) + 6CO_2 + 6H^+. \quad (56)$$

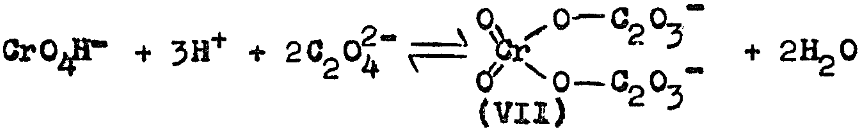
Hason and Roček[115,116] have reported in a recent study the three-electron reduction of chromium(VI) by oxalic acid, in the range of about 0.1M to 2.4M perchloric acid solution. The mechanism presented was very complex. The first step involves the formation of a neutral complex intermediate (VI).

VI



The second step is a bimolecular reaction resulting in the formation of a dioxalato complex. This complex decomposes in the rate determining step to yield a hexaquochromium(III) ion, three molecules of carbon dioxide and a $\cdot CO_2H$ free radical. This rate determining step is a one-step three electron oxidation. In the absence of a free radical scavenger, acrylamide, the free radical species will react with a chromium(VI) species to yield carbon dioxide and a chromium(V) complex which can then react further with oxalic acid. Durham[113] has also studied the kinetics and mechanism of the chromium(VI) oxidation of oxalic. The important steps were postulated to involve the formation of 1 : 1 and 1 : 2 complex intermediates and the decomposition of these species to form the products.


(VI) (57)

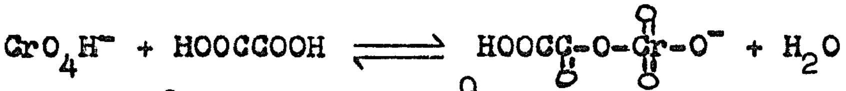

(VII) (58)

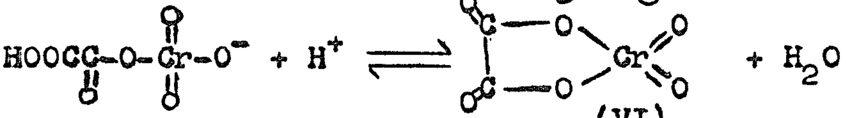
$$\text{intermediate (VI)} \longrightarrow Cr(IV) + 2CO_2 \qquad (59)$$

$$\text{intermediate (VII)} \longrightarrow Cr(IV)ox. + 2CO_2 \qquad (60)$$

However, Mason and Roček[116] point out that Durham's calculated rate constants differ greatly from those found by Bakore and Jain.[112] This may indicate that the mechanisms presented are questionable. The kinetics and mechanism for this reaction have been studied by other workers.[128]

Granzow, Wilson and Ramirez[114] have examined the chromium(VI) oxidation of the dye Malachite green in the presence of oxalic acid. The following equilibria were found to be important in the reaction mechanism.


$$CrO_4H^- + HOOCCOOH \rightleftharpoons HOOC\overset{}{\underset{\|}{\underset{O}{C}}}-O-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{Cr}}}-O^- + H_2O \qquad (61)$$


(VI) (62)

The complex intermediate, (VI), reacts with the Malachite green to yield the other reaction products. The reaction scheme presented by these workers is quite complex in that many reactive intermediates are formed.

The oxidation of oxalic acid by permanganate has been the subject of research for over a century. The mechanism for the reaction is still not completely resolved.[117] The stoichiometry for the reaction is generally accepted to be

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O \quad (63)$$

Alder and Noyes[118a] suggest that the reaction was initiated by the oxidation of a manganese(II)-oxalate complex by the permanganate ion,

$$MnO_4^- + MnC_2O_4 \longrightarrow MnO_4^{2-} + MnC_2O_4^+ \quad (64)$$

to form the manganate ion, MnO_4^{2-}. If the manganese(II) species is present in significant concentration the subsequent steps are

$$Mn(VI) + Mn(II) \rightleftharpoons 2Mn(IV) \quad (65)$$

$$Mn(IV) + Mn(II) \rightleftharpoons 2Mn(III) \quad (66)$$

If the manganese(II) ion is not present in appreciable amounts the steps are

$$Mn(VI) + C_2O_4^{2-} \longrightarrow Mn(IV) + 2CO_2 \quad (67)$$

$$2Mn(IV) + C_2O_4^{2-} \longrightarrow 2Mn(III) + 2CO_2 \quad (68)$$

The manganese(III) species subsequently reacts according to the sequence

$$Mn(C_2O_4)_n^{3-2n} \longrightarrow Mn(II) + (n-1)(C_2O_4^{2-}) + CO_2 + CO_2^{\circ -} \quad (69)$$

$$Mn(C_2O_4)_n^{3-2n} + CO_2^{\circ -} \longrightarrow Mn(II) + nC_2O_4^{2-} + CO_2 \quad (70)$$

Where n may be 1,2 or 3. At very low concentrations of oxalate the permanganate ion can also react as follows,

$$MnO_4^- + MnC_2O_4^+ \longrightarrow MnO_4^{2-} + MnC_2O_4^{2+} \quad (71)$$

The kinetics of the uncatalyzed oxidation of oxalate by peroxodisulfate has been studied by Po.[119] The reaction involves the homolytic scission of the oxygen to oxygen bond of the peroxodisulfate ion. This produces two sulfate radical ions for the chain initiating step. The chain propagation involves the oxidation of water molecules by the sulfate radical ions with the formation of a hydroxyl radical. This free radical species subsequently reacts with the oxalate ion producing the carboxyl radical ion. This radical ion attacks another peroxodisulfate ion producing another sulfate radical ion. The chain terminating step involves the oxidation of the carboxyl radical ion by the sulfate radical ion with the production of carbon dioxide and the sulfate ion. The oxidation of oxalate by peroxodisulfate has been found to be catalyzed by silver(I) ions.[129] Bhakuni and Srivastava[120] and Kalb and Allen[121] have studied the reaction between peroxodisulfate and oxalic acid catalyzed by silver(I). The chain initiating step(s) is analogous to that found by Po. The significant difference is that the sulfate radical ion oxidizes silver(I) to silver(II). The silver(II) produced reacts with the oxalate dianion, $C_2O_4^{2-}$, yielding silver(I), carbon dioxide and the carboxyl radical ion. The chain terminating steps are:

$$2CO_2^{\cdot -} \longrightarrow C_2O_4^{2-} \qquad (72)$$

$$CO_2^{\cdot -} + Ag^{+} \rightarrow CO_2 + Ag^{0} \ . \qquad (73)$$

Lead tetraacetate [106] oxidizes oxalic acid to carbon dioxide but the reaction does not go to completion since insoluble lead(II) oxalate precipitates.

The studies previously described indicate that there exists a wealth of information about the reaction pathways of formic acid and oxalic acid with numerous oxidants. To date, Kustin and coworkers[42] have reported the only other study of the silver(II) oxidation of organic substrates, namely O-methylhydroxylamine and N-methylhydroxylamine. It is the intent of this study to investigate the silver(II) oxidation of a simple monocarboxylic acid and a simple dicarboxylic acid. In view of the limited amount of kinetic studies involving reactions of silver(II) with organic substrates, this work will add considerable knowledge to the field of inorganic reaction mechanisms by providing additional insight into the electron transfer processes involving silver(II).

EXPERIMENTAL SECTION

Materials: All chemicals used were either reagent grade or of certified purity, unless otherwise noted.

High purity silver(II) oxide was obtained from Alfa Inorganics, Ventron Corp.. Formic acid solutions (90.3%), nitric acid solutions (69-71%), and cerium(III) nitrate were obtained from the Fisher Chemical Co.. Oxalic acid and silver(I) nitrate were obtained from the Amend Drug and Chemical Co.. Perchloric acid solutions(70-72%) were obtained from the J.T.Baker Chemical Co.. Sodium nitrate was obtained from the Mallinckrodt Chemical Co.. Sodium perchlorate and cerium(IV) ammonium nitrate were obtained from the G.Frederick Smith Chemical Co.. Electrophoresis grade acrylamide (CH_2=$CHCONH_2$) was obtained from the Sigma Chemical Co..

Methods of Preparation: Silver(II) solutions were prepared immediately before use for all kinetic determinations. The solutions were prepared by weighing out silver(II) oxide into twenty-five milliliter volumetric flasks. The appropriate, thermostated solvent was then added to the flask and the resultant concentration of silver(II) was determined just prior to the kinetic experiment.

All formic acid solutions were prepared from stock solutions made up just prior to use in the appropriate solvent. Similarly, all oxalic acid solutions were prepared just prior to the experiment from fresh stock solutions. These stock solutions were prepared by adding accurately weighed amounts of oxalic acid into the appropriately acidified solution.

In the kinetic experiments where the effect of silver(I) was examined, silver(I) nitrate solutions were prepared in the required solvent and the silver(II) oxide was then dissolved in these solutions. The order of addition of silver(I) nitrate in the different oxidation studies was of no consequence.

All acidic solutions were prepared using previously standardized stock solutions of nitric acid and/or perchloric acid.[130]

All solutions were prepared using distilled water from a Barnstead Still Apparatus. Various experiments showed that trace amounts of impurities such as dissolved carbonates and/or oxygen, in the distilled water had no effect on the observed kinetics of the reactions studied.

Determination of Silver(II) Concentration: The spectra of silver(II) in nitric acid and perchloric acid solution, shown in Fig. (1), were obtained using a Cary 14H Recording Spectrophotometer. The wavelengths used to study the reaction kinetics, for both studies, were 365nm ($\epsilon = 2068 \pm 39 M^{-1} cm^{-1}$) and 685nm ($\epsilon = 269 \pm 4 M^{-1} cm^{-1}$). The molar absorptivities were determined in 6.11M nitric acid solution.[23]

The method used to determine the silver(II) concentration in acid media, rapidly and accurately, has been previously reported.[1,5,47] The procedure involves taking aliquot portions of silver(II) solution and adding this solution to a given volume of 0.15M cerium(III) nitrate solution. Silver(II) oxidizes cerium(III) quantitatively to cerium(IV) via the

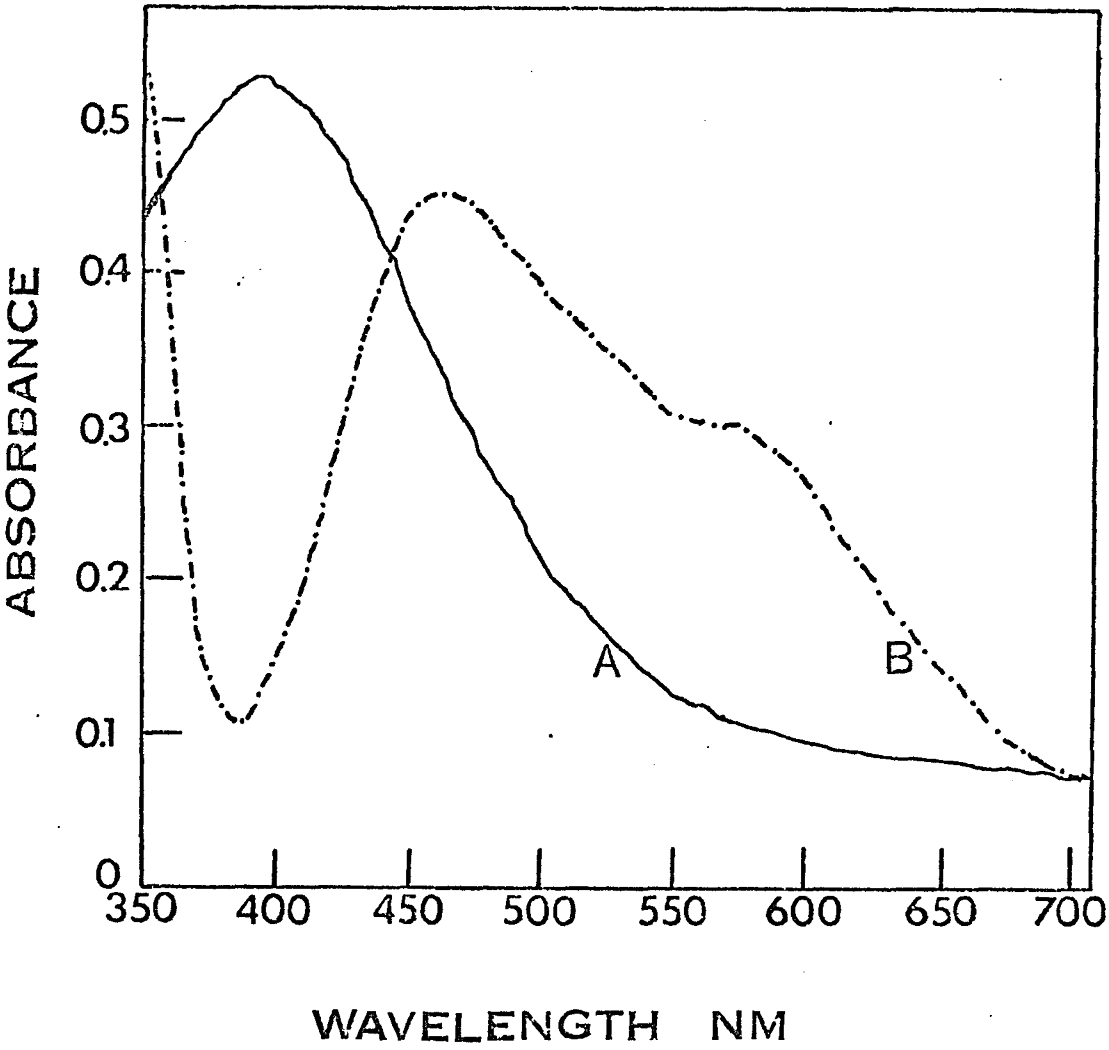


Fig. 1 Absorption Spectra of Silver(II)

A. 0.25 x 10^{-3} M Silver(II) in 6.1 M nitric acid

B. 3.3 x 10^{-3} M Silver(II) in 5.9 M perchloric acid following reaction.[15,44,47]

$$Ag(II) + Ce(III) \longrightarrow Ag(I) + Ce(IV) \qquad (74)$$

The resultant absorbance, due to the cerium(IV) produced from this reaction, is promptly measured on a spectrophotometer (i.e. Beckman DU). The absorbance recorded can be related to the concentration of cerium(IV) through a Beer's Law Curve. Once the cerium(IV) concentration is determined the silver(II) concentration is back-calculated.

Determination of Stoichiometry: The stoichiometry of the oxidation of formic acid and oxalic acid by silver(II) was determined using a Dual Buret Gas Analysis Apparatus.*
This apparatus was used to measure carbon dioxide evolution. The procedure involved adding specific volumes (40.0ml) of either organic acid to a weighed portion of silver(II) oxide in a thermostated reaction chamber. All gas evolution experiments reported were repeated using blank solutions(i.e. solvent without formic acid or oxalic acid) run against silver(II). It was found that there was negligible oxidation of the solvent by silver(II) during the time of each experiment.

Kinetic Instrumentation: The rapidity of the reaction of silver(II) with formic acid and oxalic acid necessitated the use of a rapid-mixing technique. The reaction kinetics reported in this work was studied using the stopped-flow technique. The Aminco - Morrow Stopped - Flow Apparatus [131,132] is schematically presented in Fig. (2). The apparatus is designed to

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* Appendix II

rapidly mix equal volumes of two solutions with an efficiency of mixing greater than 98% at the point of observation in less than one millisecond after the mixing is initiated.

The reactant solutions are stored in separate driving syringes. A nitrogen gas operated plunger allows the simultaneous advancement of these driving syringes forcing about 0.1 ml of each solution through a specially designed mixing chamber. After mixing has occurred the reaction mixture enters an 0.8 cm observation cell fitted with two quartz windows. This cell requires 0.04 ml of solution. Each time a kinetic run is completed a total of 0.2 ml of solution has been flushed through the cell, i.e. the equivalent of five rinsings with the reactant solutions is achieved for each kinetic run.* The reaction mixture flows through the observation cell until it enters an exhaust chamber and advances the piston of a stopping syringe to a preset micrometer stopping block. This action closes a switch which triggers the storage oscilloscope. The time required for the reaction mixture to reach the point of observation from the point of mixing is called the dead time. The dead time for this system is about two milliseconds at 70 psi of driving pressure and a micrometer setting of 3.5. All components in the stopped-flow apparatus which come in contact with any solutions are made of chemically inert materials such as Kel-F and teflon. The solutions are thermostated in the driving syringes and in the mixing chamber and observation cell by the circulation of a water-ethylene glycol solution through holes drilled into the aluminum block of the

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* In <u>all</u> cases <u>equal volumes</u> of each reactant are mixed before the resultant solution reaches the observation chamber.

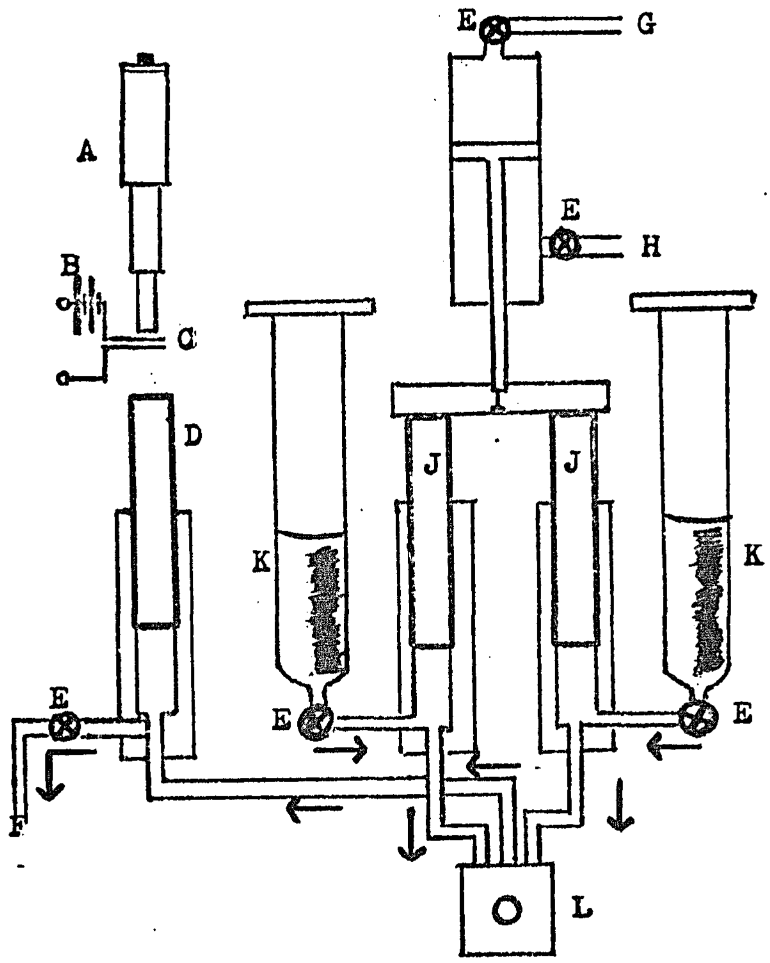

Fig. 2 Schematic Diagram of an Aminco - Morrow Stopped - Flow Apparatus (not to scale)

A. Micrometer (set at 3.5)
B. Fourteen volt miniature mercury battery
C. Trigger Switch
D. Stopping Piston
E. Valve
F. Exhaust Outlet
G. Nitrogen Gas Inlet (Advance)
H. Nitrogen Gas Inlet (Retract)
I. Plunger (Nitrogen Supply Actuator)
J. Drive Piston
K. Reactant Solution Reservoir Syringes
L. Mixing Chamber and Observation Cell

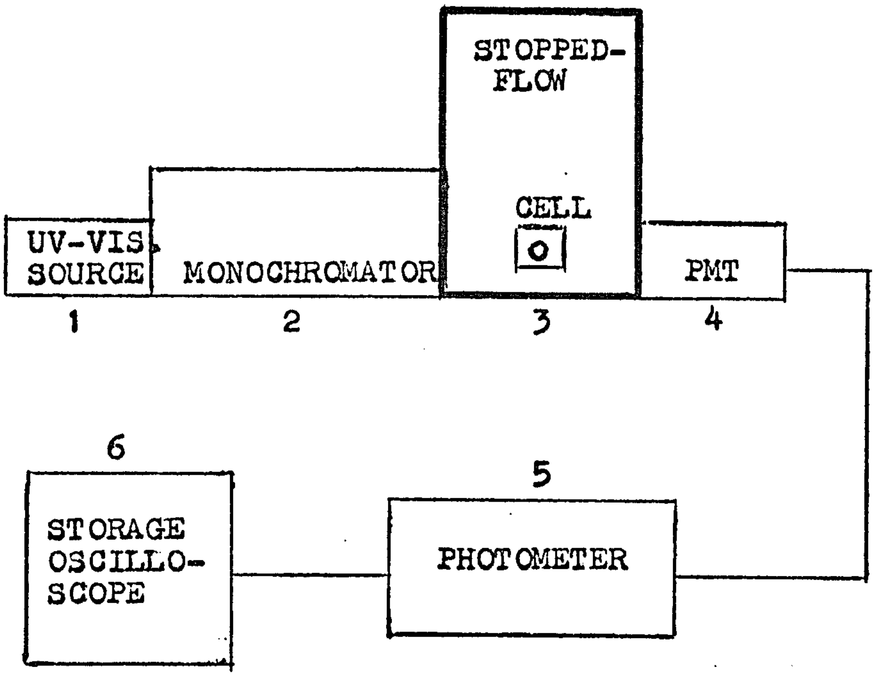

Fig. 3 Schematic Diagram of the Experimental System

1. The light source is a tungsten lamp powered by a Hewlett-Packard 6274 DC Power Supply.
2. The Aminco Minimonochromator is used in this system.
3. The mixing system is an Aminco - Morrow Stopped - Flow Apparatus.
4. The detector is an Hamamatsu R-136 Photomultiplier Tube (PMT) powered by an Aminco Photomultiplier High Voltage Power Supply.
5. The PMT output signal is fed into an Aminco Linear -Log High Performance Kinetic Photometer. This photometer permits offsetting, change of bandwidth, and selection of output as percent transmittance or as absorbance.
6. The change in absorbance with time is displayed on a Tektronix 5103N Storage Oscilloscope.

apparatus and copper tubing surrounding the mixing chamber and observation cell.

An Aminco Minimonochromator was used in conjunction with the stopped-flow apparatus to monitor the reaction at a preset wavelength. The source was a tungsten lamp which was powered by a Hewlett-Packard 6274 DC Power Supply. The detector used to follow the change in transmitted light was a Hamamatsu R-136 Photomultiplier Tube (PMT), powered by an Aminco Photomultiplier High Voltage Power Supply. The PMT output signal is fed into an Aminco Linear-Log High Performance Kinetic Photometer. The logarithmic signal, which is directly related to the absorbance, is displayed on a Tektronix 5103 N Storage Oscilloscope. A Polaroid Oscilloscope Camera (model C-5) was used to photograph the stored kinetic traces for future analysis.* Fig. (3) shows the stopped-flow apparatus and the associated electronic equipment.

Experimental Kinetic Conditions: All kinetic experiments, for the formic acid-silver(II) reaction, were performed at 25.0° ± 0.1° C, unless otherwise stated.

The concentration ranges used in various kinetic experiments at 25 °C and about 6M ionic strength were as follows:

$[HCO_2H]_T$ = $0.838 \times 10^{-2}M - 47.9 \times 10^{-2}M$

$[Ag(II)]$ = $0.404 \times 10^{-3}M - 9.74 \times 10^{-3}M$

$[Ag(I)]$ = $0.00 - 40.0 \times 10^{-3}M$

$[HNO_3]$ = $0.711M - 6.28M$

$[ClO_4^-]$ = $0.00 - 5.50M$

$[NO_3^-]$ = $0.50M - 6.3M$

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* note: typical kinetic traces are given in Fig. 8-10, 19-21.

All kinetic experiments, for the oxalic acid-silver(II), were performed at 5.0° ± 0.1 °C, unless otherwise stated.

The concentration ranges used in various kinetic experiments at 5 °C and about 6M ionic strength were as follows:

$[H_2C_2O_4]_T$ = 5.60×10^{-5}M - 5.41×10^{-3}M

$[Ag(II)]$ = 7.90×10^{-5}M - 2.57×10^{-3}M

$[Ag(I)]$ = $0.00 - 1.76 \times 10^{-2}$M

$[HNO_3]$ = 2.16M - 6.03M

$[ClO_4^-]$ = 0.00 - 5.49M

$[NO_3^-]$ = 0.500M - 6.04M

Experiments to Detect Free Radical Intermediates: Acrylamide, a free radical scavenger, was used to detect free radical intermediates produced in the reactions studied. The method used in these experiments has been reported by Hasan and Roček.[115,116] Formic acid and oxalic acid solutions were made up with acrylamide present in varying concentrations. The experiments described in the Determination of Stoichiometry section were then repeated with acrylamide at 25 °C.

Attempts were made to detect free radical species produced in the reaction of silver(II) with formic acid and oxalic acid using e.s.r. techniques. A JEOL LTD. JES-SM-1 Continuous Flow System with an aqueous flow cell (JES-LC-01) was used in conjunction with a JES 3X JEOL e.s.r. spectrometer. The Continuous Flow System was used to affect rapid mixing of the two reactants. The continuous flow of the mixed reactants was then monitored by the e.s.r. spectrometer. The experiments were performed at 0 °C and 25 °C under a wide range of kinetic conditions.

The field was calibrated using α, α'-diphenyl-β-picryl-hydrazyl (DPPH).

Temperature Study Experiments: For the formic acid-silver(II) reaction, the procedure involved preparing plots of the appropriate rate constant versus 1 / $[H^+]$ at numerous temperatures (i.e. 10°, 20°, 25°, 30°, 40° C) at constant nitrate ion concentration and ionic strength.*

For the oxalic acid-silver(II) reaction the procedure involved preparing plots of the appropriate rate constant versus 1 / $[H^+]$ at numerous temperatures (i.e. -2°, 1°, 5°, 9°, 13° C) at constant ionic strength.*

Ionic Strength Experiments: For the formic acid-silver(II) reaction the effect of ionic strength, I, was studied by varying the perchlorate ion concentration at constant nitric acid, formic acid and silver(II) concentration. The effect on the observed rate constant with varying ionic strength was examined.

For the oxalic acid-silver(II) reaction the effect of ionic strength, I, was studied by varying the nitrate ion concentration at constant nitric acid, oxalic acid and silver(II) concentration. The effect on the observed rate constant with varying ionic strength was examined.

Determination of the Equilibrium Constants for Oxalic Acid:

The equilibrium constants for oxalic acid (i.e. K_{95} and K_{96}) were determined experimentally because the reaction was

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* Appendix III

studied under conditions of high ionic strengths and low temperatures.

The equilibrium constants for oxalic acid were determined at 5°C and 25°C and 6.3M ionic strength.* The procedure involved a potentiometric titration of an aqueous solution of 0.0255M oxalic acid with a standardized sodium hydroxide solution. A Leeds and Northrup pH meter was used in conjunction with a Thomas Combination Electrode. Buffer solutions were obtained from the Fisher Scientific Co.. These solutions were used to calibrate the pH meter at 5°C and 25°C.

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* Appendix IV

RESULTS SECTION

I. THE FORMIC ACID - SILVER(II)

Stoichiometry: The results in Table (I) are consistent with the reaction

$$2Ag(II) + HCO_2H \longrightarrow 2Ag(I) + CO_2 + 2H^+ . \qquad (75)$$

The stoichiometry was determined under conditions similar to that established for the kinetic experiments. In all determinations the mole ratio of carbon dioxide to silver(II) consumed was found to be 1 : 2. Analogous stoichiometric results have been previously found for the oxidation of formic acid by most other inorganic oxidants.[72-75,77-79,81,83,88,98]

Kinetics: The loss of silver(II) was monitored using the stopped-flow apparatus. The reaction was studied under pseudo-order conditions[133] with the silver(II) species in limiting quantity. The half-life method was used in the analysis of the kinetic data.[134]

In a number of cases the kinetics were followed from 350nm to 700nm for identical reaction mixtures. Invariably the shape of the kinetic traces and the calculated rate constants were found to be identical. This indicates that the same process was being observed at all wavelengths.

The temperature was maintained at 25.0° ± 0.1° C for all kinetic runs, unless otherwise noted. The ionic strength for all the experiments was fixed at ~6.3M.

Silver(II) Dependence: Under the experimental kinetic conditions the reaction was found to have constant half-lifes,

$t_{\frac{1}{2}}$, for at least three half-lifes, at constant formic acid concentration and acidity. The constancy of the observed pseudo-order rate constant, k_{OBSD}, over a twenty-four fold concentration range indicates that the reaction is first-order in silver(II) (Table(II)). The observed pseudo-order rate constant is defined by equation(I).

$$-d[Ag(II)] / dt = k_{OBSD}[Ag(II)] \qquad (I)$$

Where $[Ag(II)]$ is the sum total of all silver(II) species in solution.

Silver(I) Dependence: The reaction rate was not affected by the addition of silver(I) to the reaction mixture. The constancy of the k_{OBSD} indicates that the reaction has a zero-order dependence on silver(I) concentration over a hundred and twenty-five fold range. (Table(III))

Formic Acid Dependence: The k_{OBSD} defined by equation (I) will be shown to contain the formic acid, hydrogen ion and nitrate ion dependencies.

The reaction was found to be first-order in formic acid over a fifty-seven fold concentration range at constant acidity and nitrate ion concentration. The data in Table (IV) indicates that k_{OBSD} is linearly dependent on the total formic acid concentration, $[HCO_2H]_T$. This relationship is shown by equation (II).

$$k_{OBSD} = k_{H,N}[HCO_2H]_T \qquad (II)$$

Where $k_{H,N}$ is a second-order rate constant incorporating both the hydrogen ion dependency and nitrate ion dependency. The plot of k_{OBSD} versus $[HCO_2H]_T$ is linear as shown in Fig. (4).

The slope, $k_{H,N}$, is 2.95 $M^{-1} sec^{-1}$ and the intercept is zero.

Acidity Dependence: At constant nitrate ion concentration the second-order rate constant, $k_{H,N}$, was found to be inversely related to the hydrogen ion concentration (Table (V)). This inverse dependency is given by equation (III).

$$k_{H,N} = A / [H^+] \qquad (III)$$

A is the proportionality constant. The plot of $k_{H,N}$ versus $1 / [H^+]$ is shown in Fig. (5). The slope, A, is 19.8 sec^{-1} and the intercept is zero in the range of 0.711M to 6.28M nitric acid.

Nitrate Ion Dependence: Table (VI) shows the effect on $k_{H,N}$ of varying the nitrate ion concentration at constant acidity. The data was found to obey equation (IV) in the nitrate ion concentration range of 0.50M to 6.0M.

$$k_{H,N} = B /(1 + K [NO_3^-]) \qquad (IV)$$

B and K are constants independent of the nitrate ion concentration. The linear form of equation (IV) is

$$1 / k_{H,N} = (K/B) [NO_3^-] + (1/B) . \qquad (V)$$

A plot of $1 / k_{H,N}$ versus $[NO_3^-]$ is shown in Fig. (6). The plot is linear with a slope, K/B , equal to 0.042 sec and an intercept, 1/B , of 0.011 M sec. The value of K calculated from graphical analysis is 3.8 ± 0.7 M^{-1}.

Temperature Study: In order to determine the thermodynamic parameters of the heat of activation, $\Delta H^{\ddagger}$, and the entropy of activation, $\Delta S^{\ddagger}$, a temperature study was undertaken for this reaction. Table(VII) contains all the calculated rate constants at each temperature. The data is plotted in Fig.(17).

TABLE I

CO_2 : Ag(II) MOLE RATIO[a,b]

moles Ag(II) $\times 10^3$	moles CO_2 $\times 10^3$	mole ratio[c] CO_2 : Ag(II)
0.289	0.15	1 : 1.9
0.291	0.15	1 : 1.9
0.298	0.16	1 : 1.9
0.438	0.21	1 : 2.1
0.954	0.48	1 : 2.0
0.954	0.49	1 : 1.9
0.955	0.49	1 : 1.9
0.955	0.49	1 : 1.9
1.89	0.96	1 : 2.0
1.89	0.96	1 : 2.0
1.89	0.98	1 : 1.9

a - All experiments were performed with $[HNO_3] = 6.18M$, $[HCO_2H]_T = 0.239M$, $I = 6.3M$ and at 25° C.

b - The total volume of the reaction mixture for each run was 40 ml..

c - The average CO_2 : Ag(II) mole ratio is 1 : 2.0 ± 0.1.

TABLE II

DEPENDENCE OF k_{OBSD} ON SILVER(II)[a,b]

$[Ag(II)] \times 10^3$	k_{OBSD}, sec^{-1}	$k_{H,N}$, $M^{-1}sec^{-1}$
0.404	0.367	3.06
0.678	0.357	2.98
1.02	0.340	2.83
1.94	0.385	3.21
2.91	0.359	2.99
3.92	0.427	3.56
5.86	0.352	2.93
6.46	0.361	3.01
8.09	0.428	3.57
9.74	0.348	2.90

a - $[HNO_3] = 6.17M$, $[HCO_2H]_T = 0.120M$ and $I = 6.3M$ for all experiments. Silver(I) was not added to the reaction mixture in these experiments.

b - The average value of $k_{H,N}$ is 3.10 ± 0.20 $M^{-1}sec^{-1}$.

TABLE III

EFFECT OF SILVER(I) ON k_{OBSD}[a,b]

[Ag(II)] x 10^3	[Ag(I)] x 10^3	k_{OBSD}, sec^{-1}	$k_{H,N}$, $M^{-1} sec^{-1}$
0.581	0.00	0.365	3.04
0.565	0.320	0.379	3.16
0.565	0.800	0.359	2.99
0.581	1.60	0.341	2.84
0.565	3.20	0.362	3.02
0.581	8.00	0.321	2.68
0.581	12.0	0.336	2.80
0.565	16.0	0.340	2.83
0.581	24.0	0.330	2.75
0.581	40.0	0.324	2.70

a - $[HNO_3] = 6.17M$, $[HCO_2H]_T = 0.120M$ and $I = 6.3M$ for all experiments.

b - The average value of $k_{H,N}$ is 2.88 ± 0.14 $M^{-1} sec^{-1}$.

TABLE IV

DEPENDENCE OF k_{OBSD} ON FORMIC ACID[a,b]

$[Ag(II)] \times 10^3$	$[HCO_2H]_T \times 10^2$	k_{OBSD}, sec^{-1}	$k_{H,N}$, $M^{-1} sec^{-1}$
0.799	0.838	0.0261	3.11
0.823	1.20	0.0374	3.12
0.823	2.39	0.0677	2.83
0.820	4.79	0.149	3.11
2.00	4.79	0.159	3.32
0.807	5.98	0.177	2.96
0.826	9.57	0.300	3.13
2.00	9.57	0.304	3.17
0.840	12.0	0.338	2.82
0.807	23.9	0.700	2.93
0.807	35.9	1.07	2.98
0.823	47.9	1.41	2.94

a - $[HNO_3] = 6.00M$ and $I = 6.3M$ for all experiments. Silver(I) was not added to the reaction mixture in these experiments.

b - The average value of $k_{H,N}$ is 3.04 ± 0.13 $M^{-1}sec^{-1}$.

TABLE V

DEPENDENCE OF $k_{H,N}$ ON THE HYDROGEN ION CONCENTRATION[a]

$[HNO_3]$	k_{OBSD}, sec^{-1}	$k_{H,N}$, $M^{-1}sec^{-1}$
0.711	3.37	28.1
1.17	2.03	16.9
1.42	1.57	13.1
1.98	1.24	10.3
2.84	0.967	8.06
3.55	0.779	6.49
3.97	0.643	5.36
4.27	0.469	3.91
4.98	0.450	3.75
5.69	0.389	3.24
6.17	0.371	3.09
6.28	0.353	2.94

a - I = 6.3M for all runs. The concentrations of formic acid and silver(II) were held constant at $[HCO_2H]_T = 0.120M$ and $[Ag(II)] = 1.7 \times 10^{-3}M$.

TABLE VI

DEPENDENCE OF $k_{H,N}$ ON THE NITRATE ION CONCENTRATION[a,b]

$[ClO_4^-]$	$[NO_3^-]$	k_{OBSD}, sec^{-1}	$k_{H,N}$, $M^{-1}sec^{-1}$
0.00	6.00	0.462	3.85
0.986	4.98	0.568	4.73
2.00	4.00	0.630	5.25
3.00	3.00	0.877	7.31
3.52	2.49	1.05	8.75
4.00	2.00	1.35	11.3
4.46	1.53	1.85	15.4
4.79	1.22	1.93	16.1
5.00	1.00	2.27	18.9
5.26	0.712	2.17	18.1
5.50	0.500	4.80	40.0

a - $[H^+]$= 6.00M and I = 6.0M for all experiments. The concentrations of formic acid and silver(II) were held constant at $[HCO_2H]_T$ = 0.120M and $[Ag(II)]$ = 1.6 x 10^{-3}M.

b - In the above experiments nitric acid and perchloric acid were both used to maintain constant acidity while allowing the nitrate ion concentration to be varied at constant ionic strength.

TABLE VII

THERMODYNAMIC DATA
FOR THE FORMIC ACID-
SILVER(II) REACTION[a]

K°	A, sec^{-1} [b]	k_{83}, M^{-1}sec^{-1} [c]	$\ln\left(\frac{h\,k_{83}}{k\,T}\right)$ [d]
283.15	7.05	1.38×10^5	-17.6
293.15	15.4	3.01×10^5	-16.8
298.15	19.8	3.87×10^5	-16.6
303.15	30.5	5.97×10^5	-16.2
313.15	64.8	12.7×10^5	-15.5

a - All experiments were performed with $[HCO_2H]_T$ = 0.120M, $[Ag(II)]$ = 2.1×10^{-3}M and I = 6.3M. The runs were made in 0.71M to 6.3M nitric acid solutions.

b- See equation (III) and equation (XVIII).

c- note: $k_{83} = k_{78}\,K_{77}$.

d- note: $h = 6.626 \times 10^{-27}$ erg sec, $k = 1.381 \times 10^{-16}$ erg °K^{-1} and T is the temperature in Kelvin degrees (K°).

TABLE VIII

DEPENDENCE OF k_{OBSD} ON FORMIC ACID IN 1M NITRIC ACID AND AT 10° C [a,b]

$[HCO_2H]_T$	k_{OBSD}, sec^{-1}	$k_{H,N}$, $M^{-1}sec^{-1}$
0.0479	0.225	4.70
0.120	0.444	3.70
0.598	2.33	3.90
1.20	4.33	3.61
2.39	8.83	3.69
3.59	15.8	4.40
4.79	21.0	4.38

a - $[HNO_3]$ = 1.0M, $[Ag(II)]$ = 2 x10^{-3}M and I = 6.3M. Silver(I) was not added to the reaction mixture in these experiments. $[NaClO_4]$ = 5.3M and all runs were made at 10 °C .

b - The average value of $k_{H,N}$ is 4.05 ± 0.38 $M^{-1}sec^{-1}$.

TABLE IX

EFFECT OF ACRYLAMIDE ON THE CO_2 : Ag(II) MOLE RATIO[a,b]

$[CH_2{=}CHCONH_2]$	moles Ag(II) x 10^3	moles CO_2 x 10^3	mole ratio CO_2 : Ag(II)
0.00	0.954	0.47	1 : 0.49
0.0499	0.947	0.33	1 : 0.35
0.0999	0.951	0.27	1 : 0.28
0.150	0.950	0.24	1 : 0.25
0.250	0.954	0.21	1 : 0.22
0.450	0.949	0.17	1 : 0.18
0.844	0.954	0.18	1 : 0.19

a - All experiments were performed with $[HNO_3] = 6.32M$, $[HCO_2H]_T = 0.479M$, $I = 6.3M$ and at 25°C.

b - The total volume of the reaction mixture for each run was 40 ml..

TABLE X

DEPENDENCE OF k_{OBSD} ON THE IONIC STRENGTH[a]

$[NaClO_4]$	I, M	k_{OBSD}, sec^{-1}
0.00	2.00	3.24
1.00	3.00	4.23
2.00	4.00	5.73
3.00	5.00	6.13
4.00	6.00	7.14

a - All experiments were performed with $[HNO_3] = 2.00M$, $[HCO_2H]_T = 0.120M$, and $[Ag(II)] = 2.5 \times 10^{-3}M$ and at 25° C.

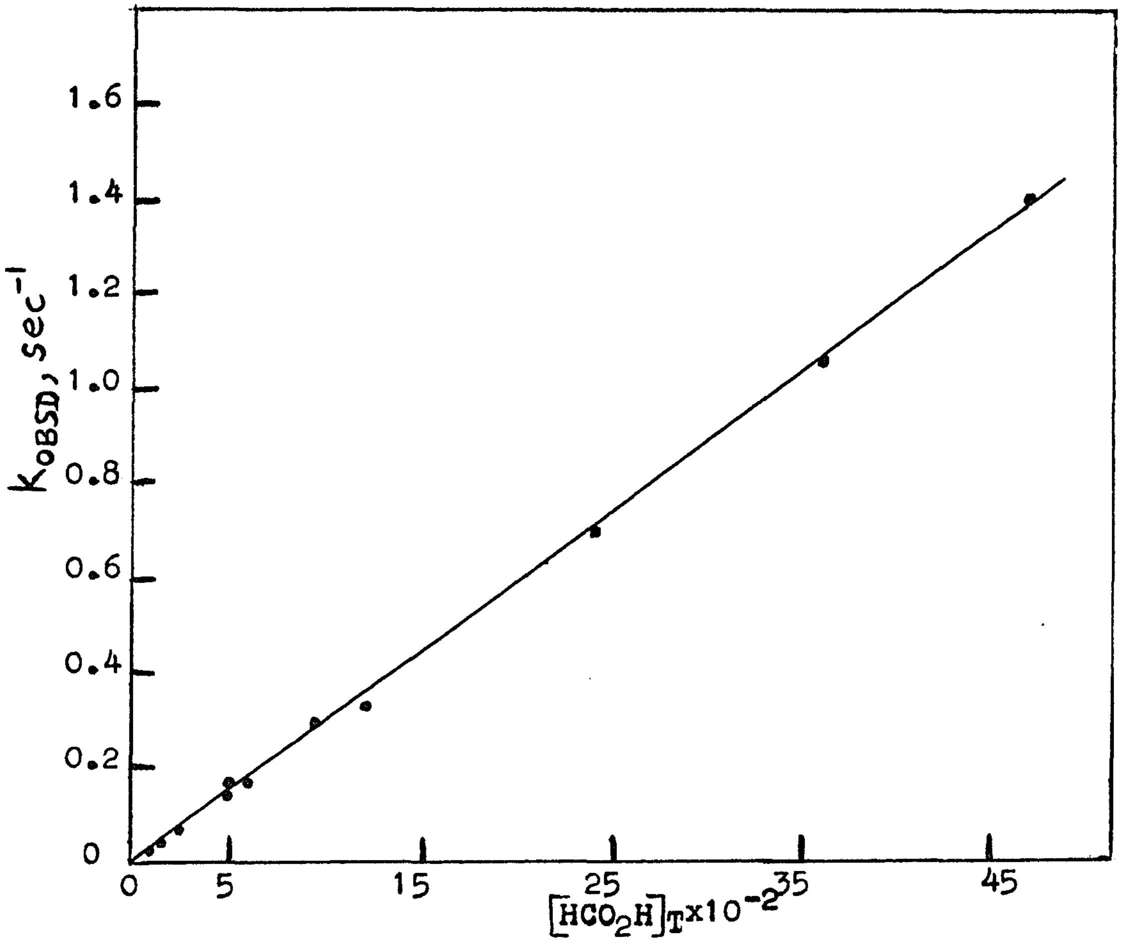

Fig. 4 Plot of k_{OBSD} vs. $[HCO_2H]_T$

This graph is based on the data in Table(IV). The equation for the straight line, calculated by the method of least-squares, is $k_{OBSD} = 2.95[HCO_2H]_T$.

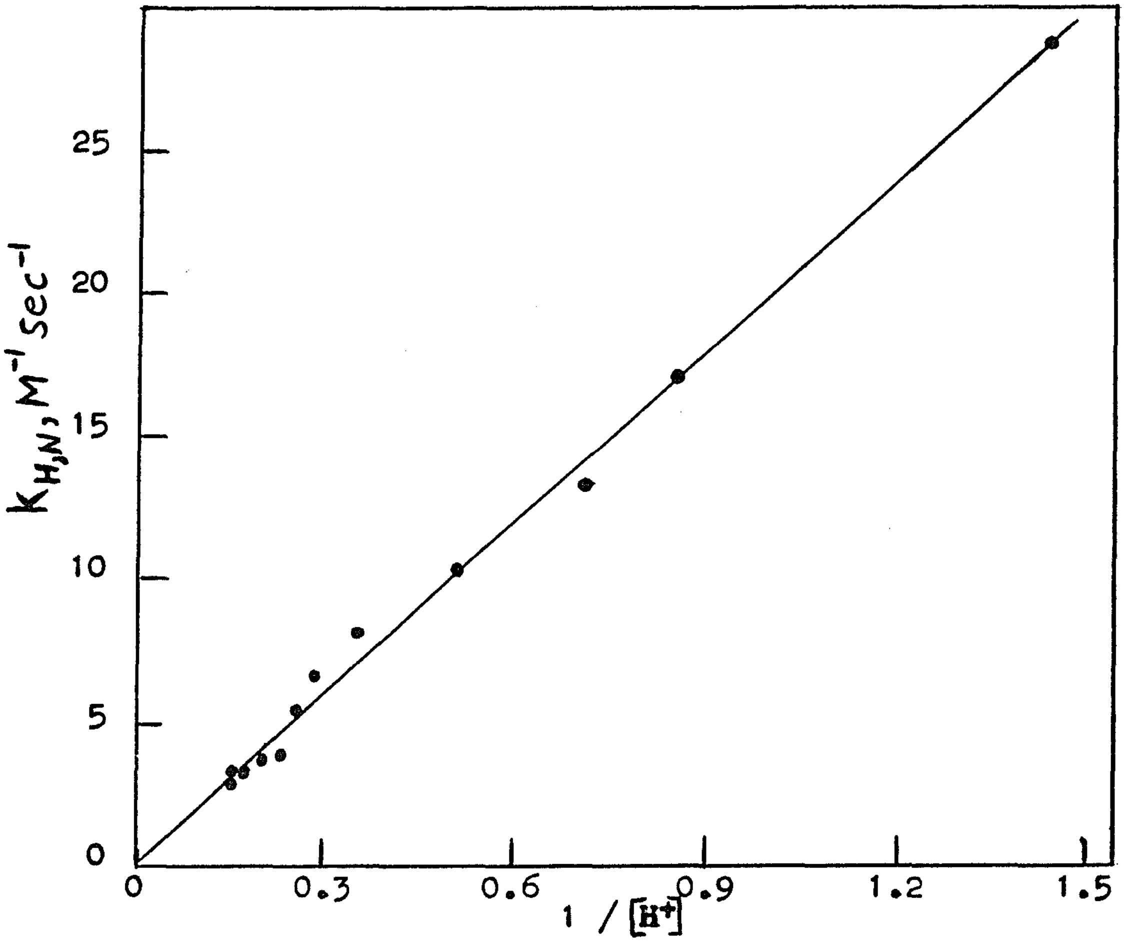

Fig. 5 Plot of $k_{H,N}$ vs. $1/[H^+]$

This graph is based on the data in Table (V). The equation for the straight line, calculated by the method of least-squares, is $k_{H,N} = 19.8\ (1/[H^+]) + 0.03$.

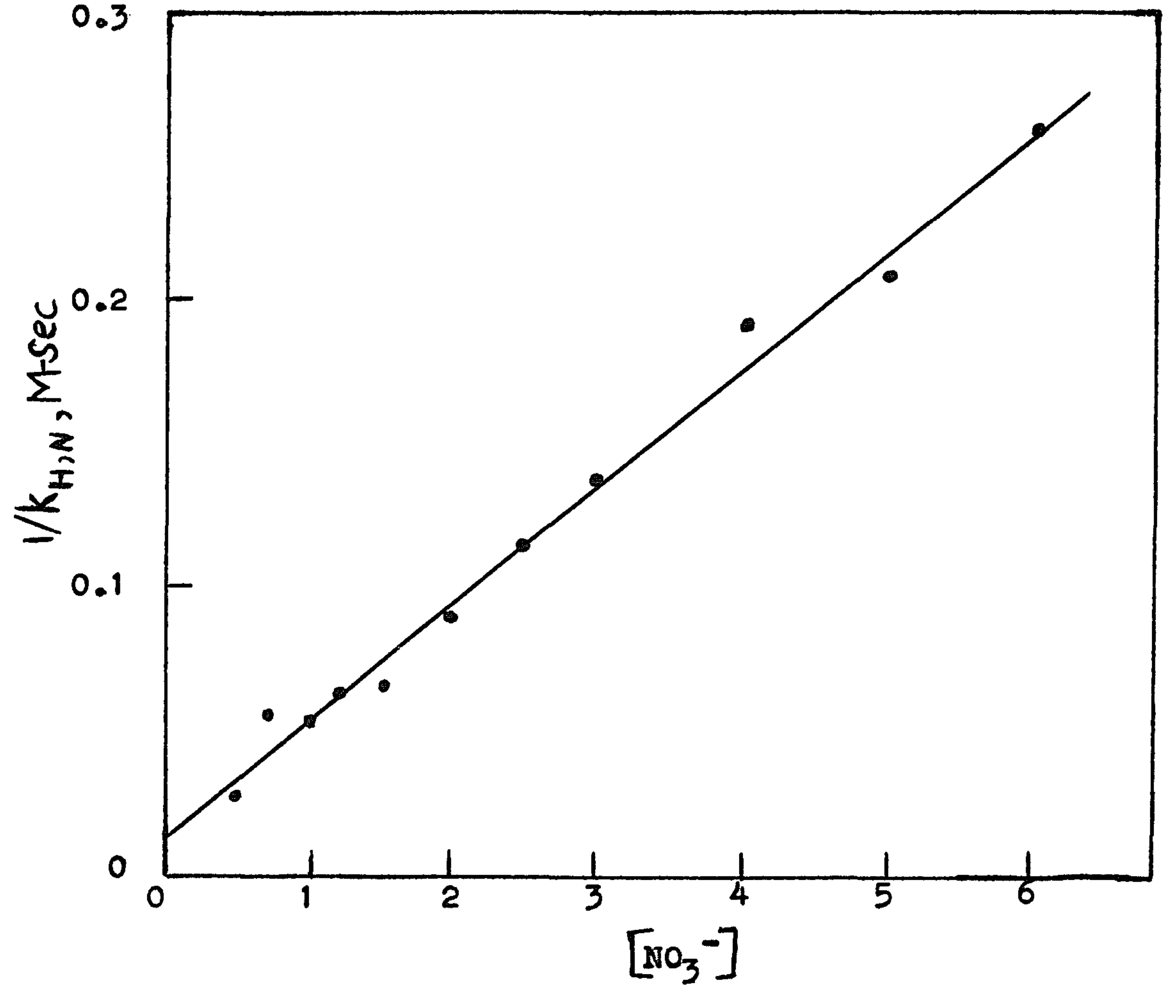

Fig. 6 Plot of $1/k_{H,N}$ vs. $[NO_3^-]$

This graph is based on the data in Table(VI). The equation for the straight line, calculated by the method of least - squares, is $1/k_{H,N} = 0.042[NO_3^-] + 0.011$. The slope is K/B and the intercept is 1/B.

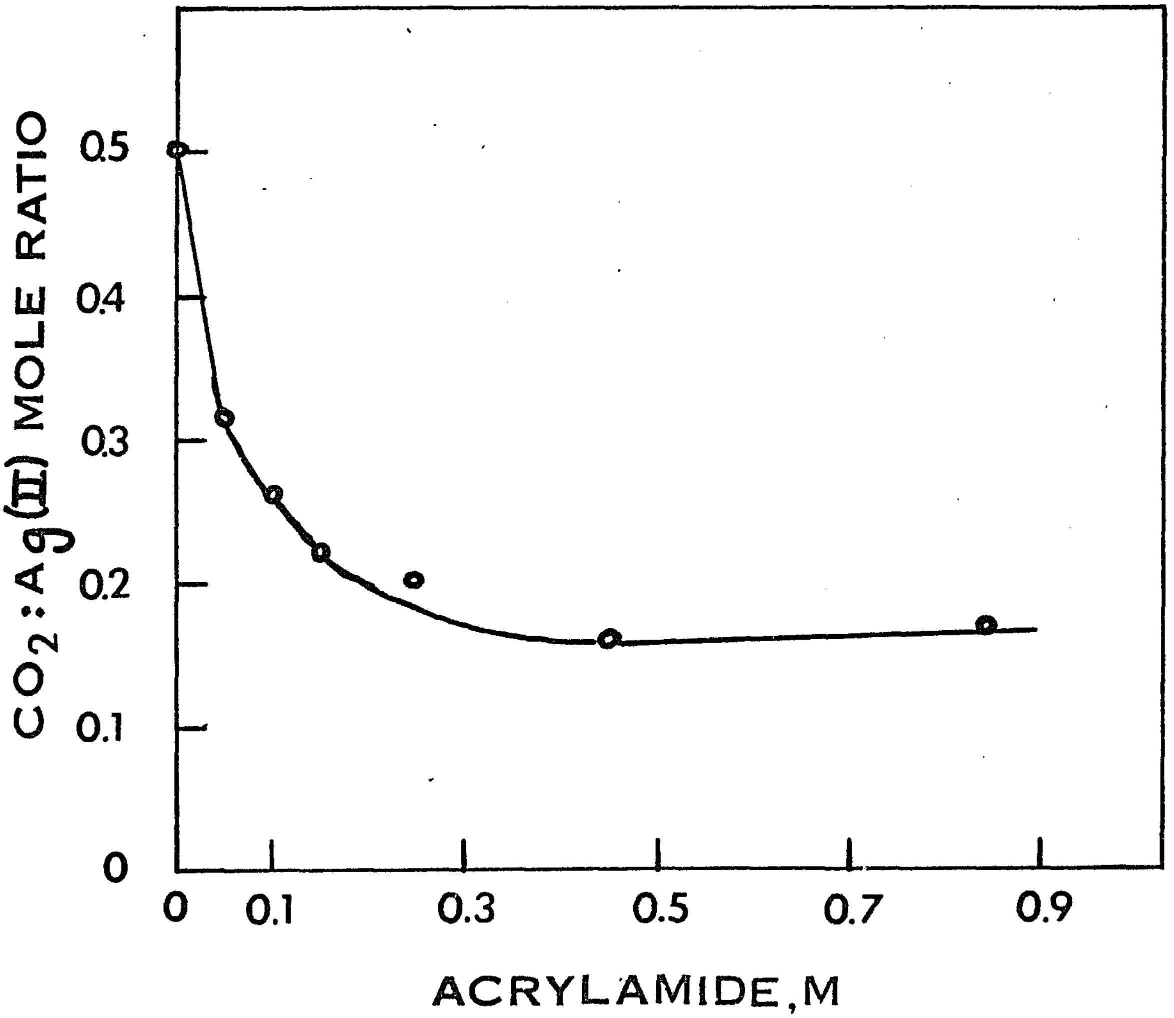

Fig. 7 Effect of Acrylamide on the CO_2:Ag(II) Mole Ratio

$[HCO_2H]_T$= 0.479 M, [Ag(II)] = 2.7×10^{-2} M, $[HNO_3]$ = 6.32 M

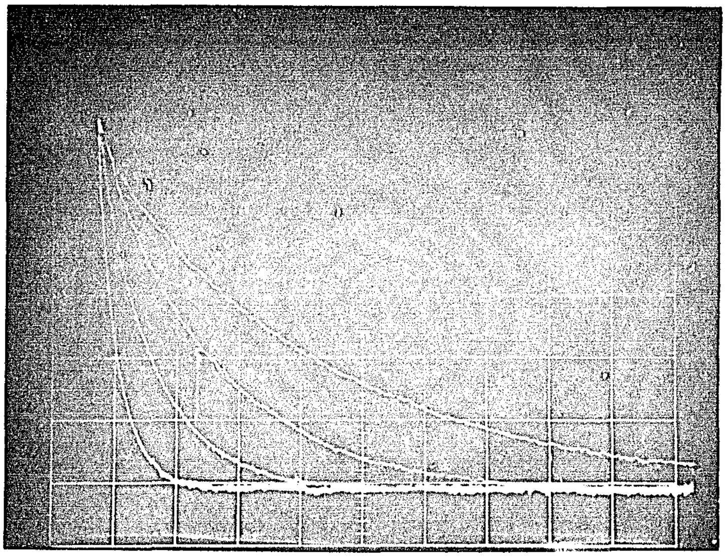

FIG. 8 TYPICAL KINETIC TRACES

Stopped - Flow conditions:

Absorbance/Div. (ordinate)	Time/Div. (abscissa)	Time Constant
0.20	0.05 sec 0.10 sec 0.20 sec 0.50 sec	0.1 msec

REACTANT A:

$[\mathrm{Ag(II)}] = 7.93\times10^{-4}$ M
$[\mathrm{Ag(I)}] = 0.00$
$[\mathrm{NaClO_4}] = 4.00$ M
$[\mathrm{HNO_3}] = 2.002$ M

REACTANT B:

$[\mathrm{HCO_2H}]_T = 0.1197$ M
$[\mathrm{NaClO_4}] = 4.00$ M
$[\mathrm{HNO_3}] = 2.002$ M

$T = 25°\mathrm{C}, \lambda = 365.0$ nm, $I = 6.0$M

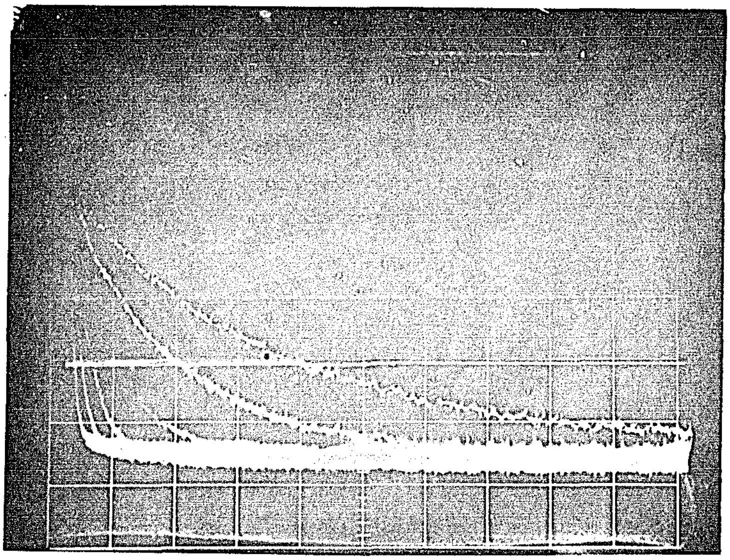

FIG. 9 TYPICAL KINETIC TRACES

Stopped - Flow conditions :

Absorbance/Div. (ordinate)	Time/Div. (abscissa)	Time Constant
0.01	0.10 sec	1.0 msec
	0.20 sec	
	0.50 sec	
	1.0 sec	
	2.0 sec	
	5.0 sec	

REACTANT A :

$[\,Ag(II)\,] = 1.68 \times 10^{-4}$
$[\,NaNO_3\,] = 5.30$ M
$[\,HNO_3\,] = 1.000$ M

REACTANT B :

$[\,HCO_2H\,]_T = 0.1203$M
$[\,NaNO_3\,] = 5.30$ M
$[\,HNO_3\,] = 1.000$ M

T = 25° C, λ = 685.0 nm, I = 6.3 M

FIG. 10 TYPICAL KINETIC TRACES

Stopped - Flow conditions:

Absorbance/Div. (ordinate)	Time/Div. (abscissa)	Time Constant
0.10	0.50 sec	0.5 msec
	1.0 sec	
	2.0 sec	
	5.0 sec	

REACTANT A:

$[\mathrm{Ag(II)}] = 5.81\times10^{-4}$ M
$[\mathrm{Ag(I)}] = 23.99\times10^{-3}$ M
$[\mathrm{NaNO_3}] = 0.130$ M
$[\mathrm{HNO_3}] = 6.167$ M

REACTANT B:

$[\mathrm{HCO_2H}]_T = 0.1197$ M
$[\mathrm{NaNO_3}] = 0.130$ M
$[\mathrm{HNO_3}] = 6.167$ M

$T = 25^\circ\mathrm{C}$, $\lambda = 365.0$ nm, $I = 6.3$ M

The calculated thermodynamic parameters are: $\Delta H^{\ddagger} = 12.3$ Kcal/mole and $\Delta S^{\ddagger} = 8.6$ cal/mole deg. .

II. THE OXALIC ACID - SILVER(II)

Stoichiometry: The results in Table (XI) are consistent with the reaction

$$2Ag(II) + H_2C_2O_4 \longrightarrow 2Ag(I) + 2CO_2 + 2H^+ . \qquad (76)$$

The stoichiometry was determined under conditions similar to that established for the kinetic experiments. In all determinations the mole ratio of carbon dioxide evolved to silver(II) consumed was found to be 1 : 1. Analogous stoichiometric results have been previously found for the oxidation of oxalic acid by many other inorganic oxidants.[103,107,109,110,112,117]

Kinetics: The loss of silver(II) was monitored using the stopped-flow apparatus. The reaction was studied under pseudo-order conditions[133] with silver(II) in limiting quantity. The half-life method was used in the analysis of the kinetic data.[134]

In a number of cases the kinetics were followed from 350nm to 700nm for identical reaction mixtures. Invariably the shape of the kinetic traces and the calculated rate constants were found to be identical indicating that the same process was being observed at all wavelengths.

The temperature was maintained at 5.0° ± 0.1° C for all kinetic runs, unless otherwise noted. The ionic strength for all experiments was fixed at ~6.0M.

Silver(II) Dependence:

A. Silver(II) in Limiting Quantity: Under the experimental kinetic conditions the reaction was found to have constant half-lifes for at least three half-lifes at constant oxalic acid concentration and acidity. The constancy of the observed pseudo-order rate constant, k'_{OBSD}, over an eight fold concentration range indicates that the reaction is first-order in silver(II). (Table(XII))

The observed rate constant is defined by equation (VI).

$$-d\left[Ag(II)\right] / dt = k'_{OBSD}\left[Ag(II)\right] \qquad (VI)$$

Where $[Ag(II)]$ represents the sum total of all silver(II) species in solution.

B. __Silver(II) in Excess Quantity over Oxalic Acid:__ The reaction was also studied where the oxalic acid was in limiting quantity. The purpose of these experiments was to give information on the stoichiometry of the reaction. The data in Table(XIII) and Table(XIV) show that there is a linear relationship between the observed rate constant, k''_{OBSD}, and $[Ag(II)]$. The rate of reaction, under these conditions, is defined by equation (VII).

$$-d\left[H_2C_2O_4\right]_T / dt = k''_{OBSD}\left[H_2C_2O_4\right]_T \qquad (VII)$$

If the stoichiometry given by reaction 76 is correct it follows that

$$-\tfrac{1}{2}\, d\left[Ag(II)\right] / dt = -d\left[H_2C_2O_4\right]_T / dt\ . \qquad (VIII)$$

The relationship between k''_{OBSD} and $[Ag(II)]$ is expressed in equation (IX).

$$k''_{OBSD} = k\left[Ag(II)\right] \qquad (IX)$$

Where k is a second-order rate constant. The plots of k''_{OBSD} versus $[Ag(II)]$ in 6M nitric acid (Fig. (11)) and in 11.8M nitric acid (Fig. (12)) are linear. The slope, k , is 0.58 x 10^5 $M^{-1}sec^{-1}$ in 6M nitric acid solution and 2.1 x 10^3 $M^{-1}sec^{-1}$ in 11.8M nitric acid solution. The intercept is zero in both plots within experimental limits.

Silver(I) Dependence: The rate of the reaction was not affected by the addition of silver(I) to the reaction mixture. The constancy of the k'_{OBSD} (Table (XV)) indicates that the reaction has a zero-order dependency on silver(I) concentration over a hundred and ninety-four fold range.

Oxalic Acid Dependence: Under conditions of limiting silver(II) the k'_{OBSD} defined by equation (VI) will be shown to contain the oxalic acid and hydrogen ion dependencies. The reaction was found to be first-order in oxalic acid over a thirteen fold concentration range at constant acidity. The data in Table(XVI) and Table (XVII) indicates that k'_{OBSD} is linearly dependent on the total oxalic acid concentration, $[H_2C_2O_4]_T$. This relationship is given by equation (X).

$$k'_{OBSD} = k_H [H_2C_2O_4]_T \qquad (X)$$

The second-order rate constant, k_H , incorporates the hydrogen ion dependency. The plots of k'_{OBSD} versus $[H_2C_2O_4]_T$ in 6M nitric acid (Fig. (13)) and in 11.8M nitric acid (Fig. (14)) are both linear. The slope, k_H , is 1.3 x 10^5 $M^{-1}sec^{-1}$ in 6M acid and 3.9 x 10^3 $M^{-1}sec^{-1}$ in 11.8M acid. The intercept is zero in both plots within experimental limits.

A comparison of k_H : k ,at the appropriate acidity (i.e. 6M or 11.8M), indicates that $k_H / 2 = k$. This means that the relationship given in equation (VIII) must be valid. It is noteworthy that these results are identical to those obtained from the gas evolution experiments (i.e. used to determine the stoichiometry).

Acidity Dependence: The second-order rate constant, k_H , is given by equation (XI). (See data in Table (XVIII)).

$$k_H = k' / [H^+] + k'' / [H^+]^2 \qquad (XI)$$

The constants k' and k'' are independent of the hydrogen ion concentration. The linear form of equation (XI) is

$$k_H [H^+] = k'' / [H^+] + k' . \qquad (XII)$$

A plot of $k_H [H^+]$ versus $1 / [H^+]$ is shown in Fig. (15). The plot is linear with a slope, k'', equal to 4.65×10^6 M sec^{-1} and an intercept, k', equal to 1.22×10^4 sec^{-1}. The acidity range of this study was 2.16M to 6.03M nitric acid. The lower value of the acidity range was set by the instrumentation used to follow the reaction, since the reaction was so rapid.

Nitrate Ion Dependence: Table (XIX) shows that in the range of concentrations studied there was no effect of the nitrate ion on the observed rate constant, k'_{OBSD}. The reaction, therefore, has a zero-order dependence on the nitrate ion concentration.

Temperature Study: The data was obtained in a manner similar to that for the formic acid-silver(II) reaction. The calculated thermodynamic parameters are given in Table (XX). The data is plotted in Fig. (18). The value of $\Delta H^{\ddagger} = 3.2$ Kcal/mole and $\Delta S^{\ddagger} = 7.0$ cal/mole deg. was calculated using the equation given in Appendix III .

TABLE XI

CO_2 : Ag(II) MOLE RATIO [a,b]

moles Ag(II) x 10^3	moles CO_2 x 10^3	mole ratio [c] CO_2 : Ag(II)
0.163	0.16	1 : 1.0
0.163	0.17	1 : 0.96
0.165	0.16	1 : 1.0
0.439	0.46	1 : 0.95
0.445	0.47	1 : 0.95
0.876	0.90	1 : 0.97
0.876	0.91	1 : 0.96
0.876	0.91	1 : 0.96
0.877	0.83	1 : 1.1
0.973	0.94	1 : 1.0

a - All experiments were performed with $[HNO_3] = 6.31M$, $[H_2C_2O_4]_T = 0.225M$, I = 6.3M and at 25° C.

b - The total volume of the reaction mixture for each run was 40 ml..

c - The average CO_2 : Ag(II) mole ratio is 1 : 0.99 ± 0.03.

TABLE XII

DEPENDENCE OF k'_{OBSD} ON SILVER(II)[a,b]

$[Ag(II)] \times 10^4$	k'_{OBSD}, sec^{-1}	k_H, $10^{-5}M^{-1}sec^{-1}$
0.790	388	1.29
1.00	364	1.21
1.36	403	1.34
1.83	385	1.28
2.44	356	1.18
2.98	376	1.25
3.51	383	1.27
4.10	391	1.30
4.79	393	1.31
5.17	377	1.25
6.09	381	1.27

a - $[HNO_3] = 5.99M$, $[H_2C_2O_4]_T = 3.01 \times 10^{-3}M$ and $I = 6.04M$ for all experiments. Silver(I) was not added to the reaction mixture in these experiments.

b - The average value of $k_H = 1.27 \pm 0.03 \times 10^5\ M^{-1}sec^{-1}$.

TABLE XIII

DEPENDENCE OF k''_{OBSD} ON SILVER(II)[a,b]

$[Ag(II)] \times 10^3$	k''_{OBSD}, sec^{-1}	$(k''_{OBSD} / [Ag(II)])$, $10^{-4} M^{-1} sec^{-1}$
0.137	8.27	6.04
0.441	26.7	6.05
0.620	40.3	6.50
0.760	42.3	5.57
0.843	54.6	6.48
0.959	66.0	6.88
0.959	70.7	7.37
1.30	73.7	5.67
1.54	100	6.49
2.01	130	6.47
2.57	144	5.60

a - $[HNO_3]$ = 5.95M, $[H_2C_2O_4]_T$ = 5.60 x 10^{-5}M and I = 6.02M for all experiments. Silver(I) was not added to the reaction mixture in these experiments.

b - The average value of $(k''_{OBSD} / [Ag(II)])$ = 6.28 ± 0.46 x 10^4 $M^{-1} sec^{-1}$.

TABLE XIV

DEPENDENCE OF k''_{OBSD} ON SILVER(II) [a,b]

$[\text{Ag(II)}] \times 10^3$	k''_{OBSD}, sec^{-1}	$(k''_{OBSD}/[\text{Ag(II)}])$, $10^{-3}\text{M}^{-1}\text{sec}^{-1}$
0.533	0.863	1.62
0.985	2.05	2.08
1.73	2.91	1.68
2.15	3.92	1.82
2.66	4.81	1.81
3.25	6.54	2.01
3.79	8.58	2.26
4.24	8.67	2.04
4.84	11.0	2.27
5.65	11.9	2.11
6.38	12.4	1.94

a - $[HNO_3] = 11.8M$, $[H_2C_2O_4]_T = 5.31 \times 10^{-5}M$ and I = 12M for all experiments. Silver(I) was not added to the reaction mixture in these experiments.

b - The average value of $(k''_{OBSD}/[\text{Ag(II)}]) = 1.97 \pm 0.18 \times 10^3\ \text{M}^{-1}\text{sec}^{-1}$.

TABLE XV

EFFECT OF SILVER(I) ON k'_{OBSD}

$[Ag(II)] \times 10^4$	$[Ag(I)] \times 10^4$	k'_{OBSD}, sec^{-1}	k_H, 10^{-5} $M^{-1}sec^{-1}$
2.71	0.00	181	1.50
1.43	0.907	176	1.45
2.70	0.907	190	1.57
3.82	0.907	183	1.51
2.77	1.81	196	1.62
2.80	2.72	178	1.47
2.75	4.54	201	1.66
2.80	9.07	213	1.76
2.76	22.7	196	1.62
2.74	45.4	205	1.69
2.73	90.7	210	1.74
2.70	176	201	1.66

a - $[HNO_3] = 5.74M$, $[H_2C_2O_4]_T = 1.21 \times 10^{-3}M$ and $I = 6.02M$ for all experiments.

b - The average value of $k_H = 1.60 \pm 0.09 \times 10^5$ $M^{-1}sec^{-1}$.

TABLE XVI

DEPENDENCE OF k'_{OBSD} ON OXALIC ACID [a,b]

$[H_2C_2O_4]_T \times 10^3$	k'_{OBSD}, sec^{-1}	k_H, 10^{-5} $M^{-1}sec^{-1}$
0.420	52	1.24
0.841	114	1.36
1.20	154	1.28
1.80	235	1.31
2.40	325	1.35
3.00	385	1.28
3.43	447	1.30
3.60	447	1.24
4.00	558	1.40
4.20	578	1.38
5.41	660	1.22

a - $[HNO_3]$ = 6.02M, $[Ag(II)]$ = 1.1×10^{-4}M and I = 6.02M for all experiments. Silver(I) was not added to the reaction mixture in these experiments.

b - The average value of $k_H = 1.31 \pm 0.05 \times 10^5\ M^{-1}sec^{-1}$.

TABLE XVII

DEPENDENCE OF k'_{OBSD} ON OXALIC ACID ^{a,b}

$[H_2C_2O_4]_T \times 10^2$	k'_{OBSD}, sec^{-1}	k_H, 10^{-3} $M^{-1}sec^{-1}$
0.225	8.99	4.00
0.375	16.2	4.32
0.751	32.1	4.27
1.13	45.9	4.06
1.43	59.2	4.14
1.50	60.3	4.02
1.88	76.2	4.05
2.25	95.1	4.23
2.63	99.9	3.80
3.00	118	3.93
3.75	148	3.95

a - $[HNO_3]$ = 11.8M, $[Ag(II)]$ = 1.9×10^{-4}M and I = 12M for all experiments. Silver(I) was not added to the reaction mixture in these experiments.

b - The average value of $k_H = 4.07 \pm 0.12 \times 10^3$ $M^{-1}sec^{-1}$.

TABLE XVIII

DEPENDENCE OF k_H ON THE HYDROGEN ION CONCENTRATION[a,b]

$[HNO_3]$	$[H_2C_2O_4]_T \times 10^3$	k'_{OBSD}, sec^{-1}	k_H, $10^{-5} M^{-1} sec^{-1}$
2.155	0.413	433	10.5
2.336	0.413	365	8.84
2.586	0.413	287	6.95
2.740	1.21	770	6.36
2.746	1.20	722	6.02
2.799	1.21	737	6.09
2.835	0.413	245	5.93
2.852	1.20	654	5.45
2.905	1.20	609	5.08
2.958	1.19	679	5.71
3.011	1.22	666	5.46
3.037	1.21	609	5.03
3.090	1.19	550	4.62
3.118	1.19	513	4.31
3.143	1.20	559	4.66
3.220	1.21	533	4.40
3.377	1.21	481	3.98
3.689	1.21	433	3.58
3.744	1.21	439	3.63
4.053	1.19	354	2.97
4.197	0.413	112	2.71
4.261	1.20	318	2.65
4.469	1.21	291	2.40
4.734	1.20	234	1.95
5.251	1.19	213	1.79
5.671	0.413	67.0	1.62
5.738	1.21	177	1.46
5.767	1.19	168	1.41
5.949	1.21	153	1.26
6.026	1.19	154	1.29
6.027	1.21	154	1.27

a - I = 6.03M for all runs. The concentration of silver(II) was held constant at $[Ag(II)] = 1.0 \times 10^{-4}$M. Silver(I) was not added to the reaction mixture in these experiments.

b - The temperature was fixed at 5° C.

TABLE XIX

EFFECT OF THE NITRATE ION ON k'_{OBSD} [a,b,c]

$[ClO_4^-]$	$[NO_3^-]$	k'_{OBSD}, sec^{-1}	k_H, 10^{-5} $M^{-1}sec^{-1}$
0.00	5.95	152	1.24
0.986	5.00	144	1.17
2.02	4.00	129	1.05
3.01	3.00	119	0.967
3.99	2.00	130	1.06
5.03	0.999	144	1.17
5.49	0.500	149	1.21

a - $[H^+]$ = 6.00M and I = 6.0M for all experiments. The concentrations of oxalic acid and silver(II) were held constant at $[H_2C_2O_4]_T = 1.23 \times 10^{-3}M$ and $[Ag(II)] = 1.4 \times 10^{-4}M$.

b - In the above experiments nitric acid and perchloric acid were both used to maintain constant acidity while allowing the nitrate ion concentration to be varied at constant ionic strength.

c - The average value of k_H is $1.12 \pm 0.08 \times 10^5$ $M^{-1}sec^{-1}$.

TABLE XX

THERMODYNAMIC DATA FOR THE OXALIC ACID-SILVER(II) REACTION [a]

K°	k'', M sec^{-1} [b]	k_{89}, $M^{-1} sec^{-1}$ [c]	$\ln\left(\frac{h\, k_{89}}{k\, T}\right)$ [d]
271.15	3.83×10^{6}	4.30×10^{11}	-2.58
274.15	4.35×10^{6}	4.89×10^{11}	-2.46
278.15	4.65×10^{6}	5.22×10^{11}	-2.41
282.15	5.00×10^{6}	5.62×10^{11}	-2.35
286.15	5.69×10^{6}	6.39×10^{11}	-2.23

a - All experiments were performed with $[H_2C_2O_4]_T$ = 4.13×10^{-4}M, $[Ag(II)]$ = 0.85×10^{-4}M and I = 6.03M. The runs were made in 3.4M to 5.9M nitric acid solutions.

b - See equation (XI) and equation (XXVIII).

c - note: The thermodynamic parameters for the k_{87} could not be determined because of large errors in the value of the intercept for plots of $k_H[H^+]$ versus $1/[H^+]$. (See equation (XII)).

d - note: $h = 6.626 \times 10^{-27}$ erg sec, $k = 1.381 \times 10^{-16}$ erg K^{-1} and T is the temperature in Kelvin degrees (K°).

TABLE XXI

EFFECT OF ACRYLAMIDE ON THE

CO_2 : Ag(II) MOLE RATIO [a,b]

$[CH_2=CHCONH_2]$	moles Ag(II) x 10^3	moles CO_2 x 10^3	mole ratio CO_2 : Ag(II)
0.00	0.974	0.94	1 : 0.97
0.0250	0.973	0.68	1 : 0.70
0.0507	0.976	0.62	1 : 0.64
0.151	0.978	0.50	1 : 0.51
0.253	0.976	0.39	1 : 0.40
0.450	0.976	0.34	1 : 0.35
0.901	0.976	0.32	1 : 0.33

a - All experiments were performed with $[HNO_3]$ = 6.32M, $[H_2C_2O_4]_T$ = 0.450M, I = 6.3M and at 25° C.

b - The total volume of the reaction mixture for each run was 40 ml..

TABLE XXII

DEPENDENCE OF k'_{OBSD} ON THE IONIC STRENGTH[a]

$[NaNO_3]$	I, M	k'_{OBSD}, sec^{-1}
0.00	3.00	866
1.01	4.01	770
2.00	5.00	541
3.00	6.00	385

a - All experiments were performed with $[HNO_3] = 3.00M$, $[H_2C_2O_4]_T = 0.635 \times 10^{-3}M$, and $[Ag(II)] = 1.2 \times 10^{-4}M$ and at 5° C.

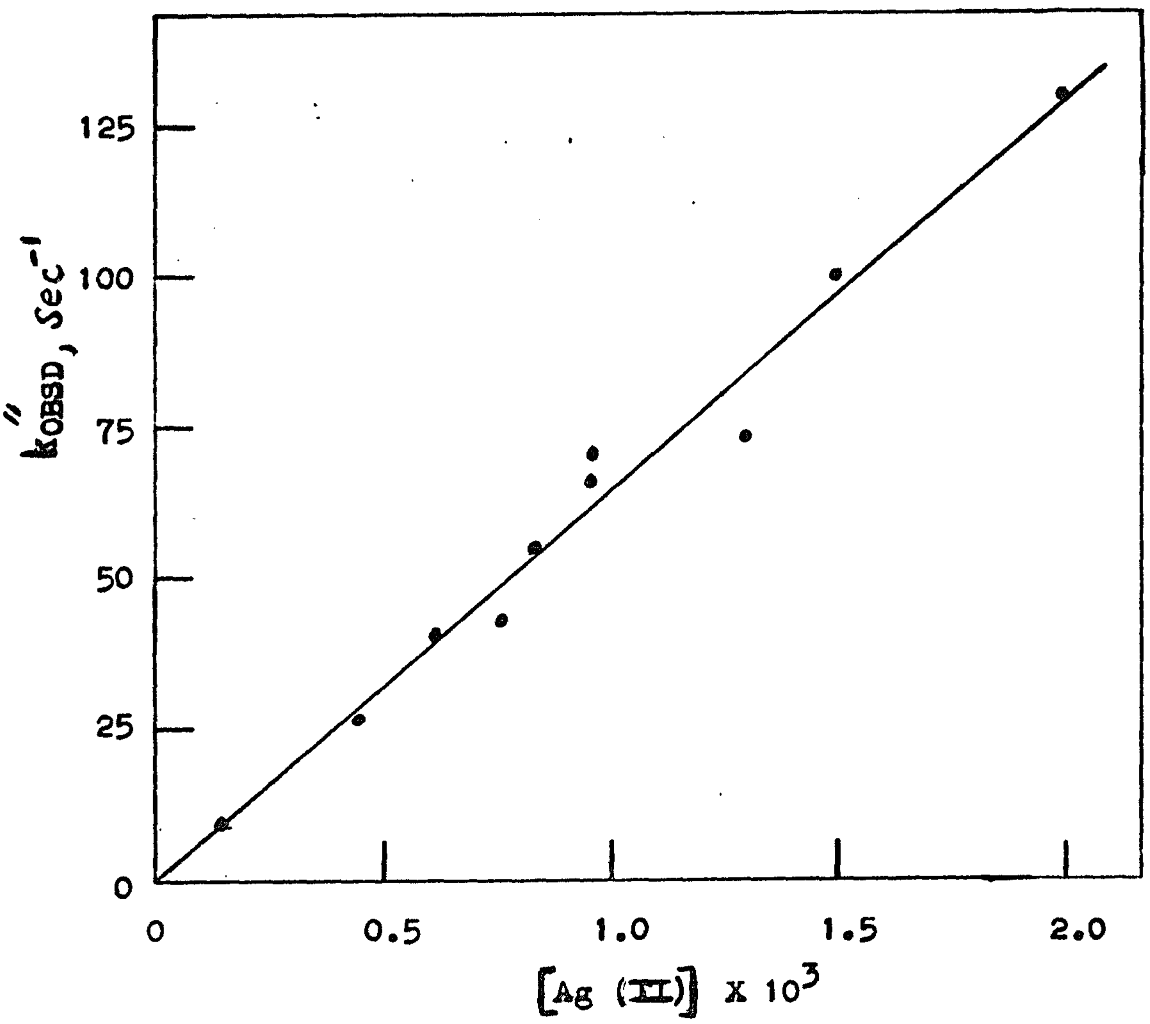

Fig. 11 Plot of k''_{OBSD} vs. [Ag(II)]

This graph is based on the data in Table (XIII). The equation for the straight line, calculated by the method of least - squares, is $k''_{OBSD} = 5.83 \times 10^4 [Ag(II)]$.

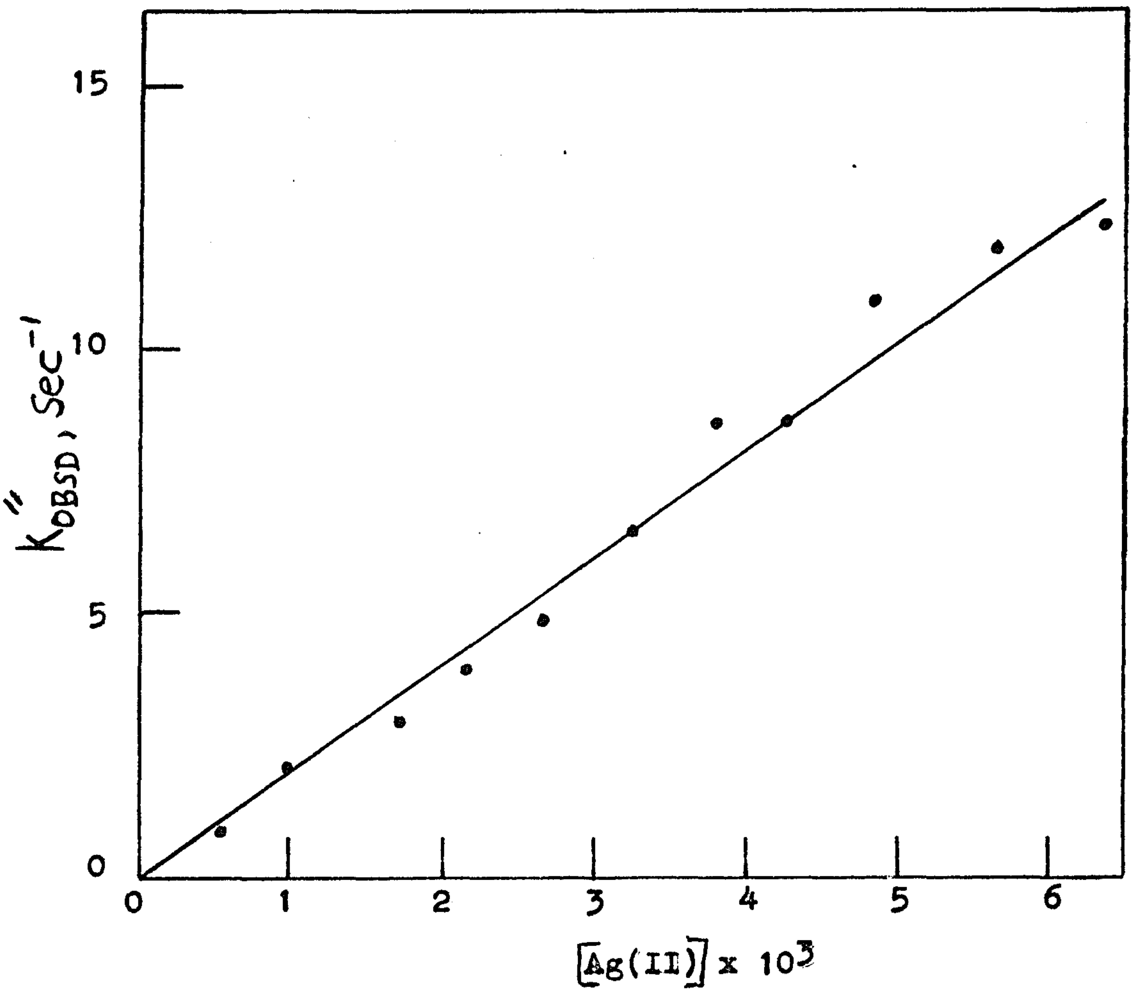

Fig. 12 Plot of k''_{OBSD} vs. $[Ag(II)]$

This graph is based on the data in Table(XIV). The equation for the straight line, calculated by the method of least - squares, is $k''_{OBSD} = 2.14 \times 10^3[Ag(II)]$.

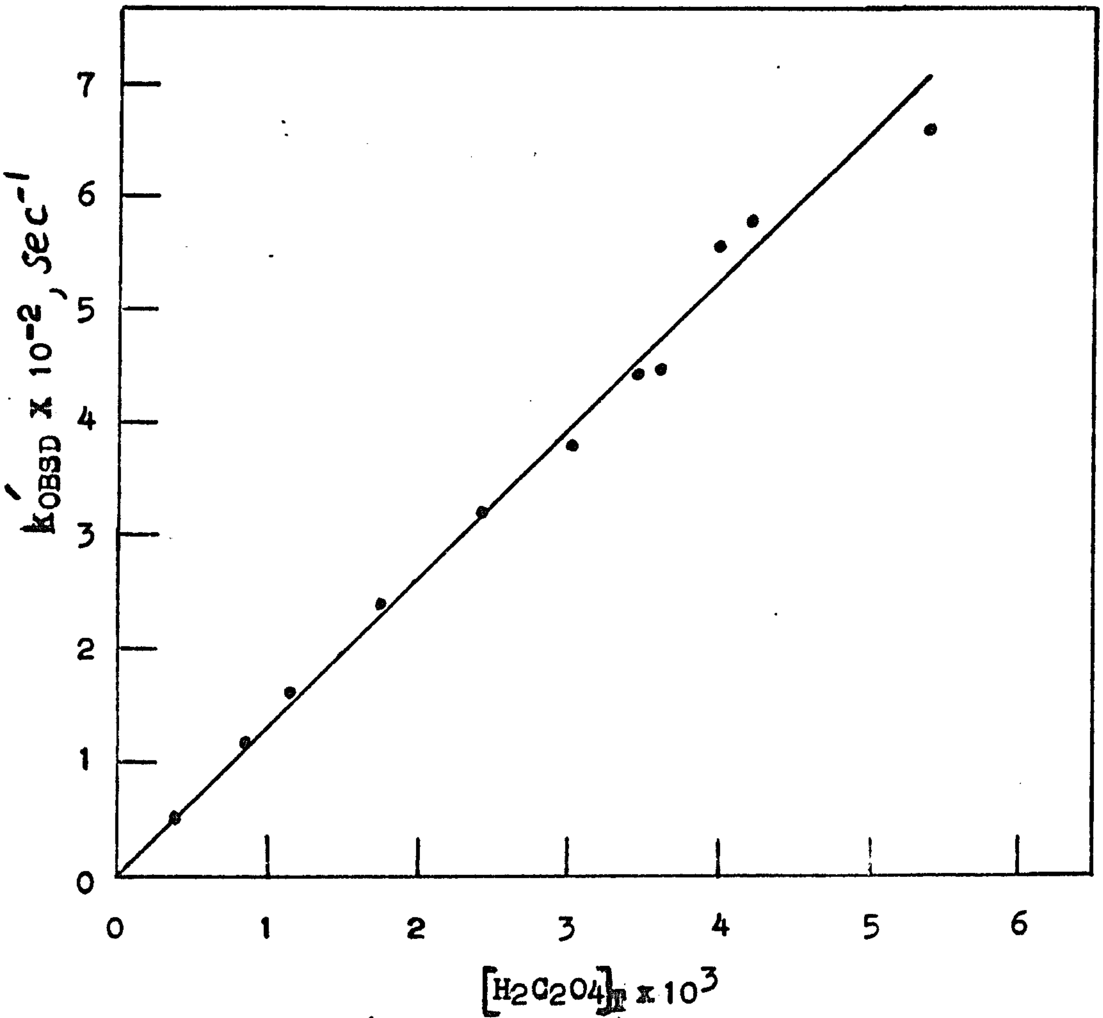

Fig. 13 Plot of k'_{OBSD} vs. $[H_2C_2O_4]_T$

This graph is based on the data in Table(XVI). The equation for the straight line, calculated by the method of least-squares, is $k'_{OBSD} = 1.28 \times 10^5 [H_2C_2O_4]_T$.

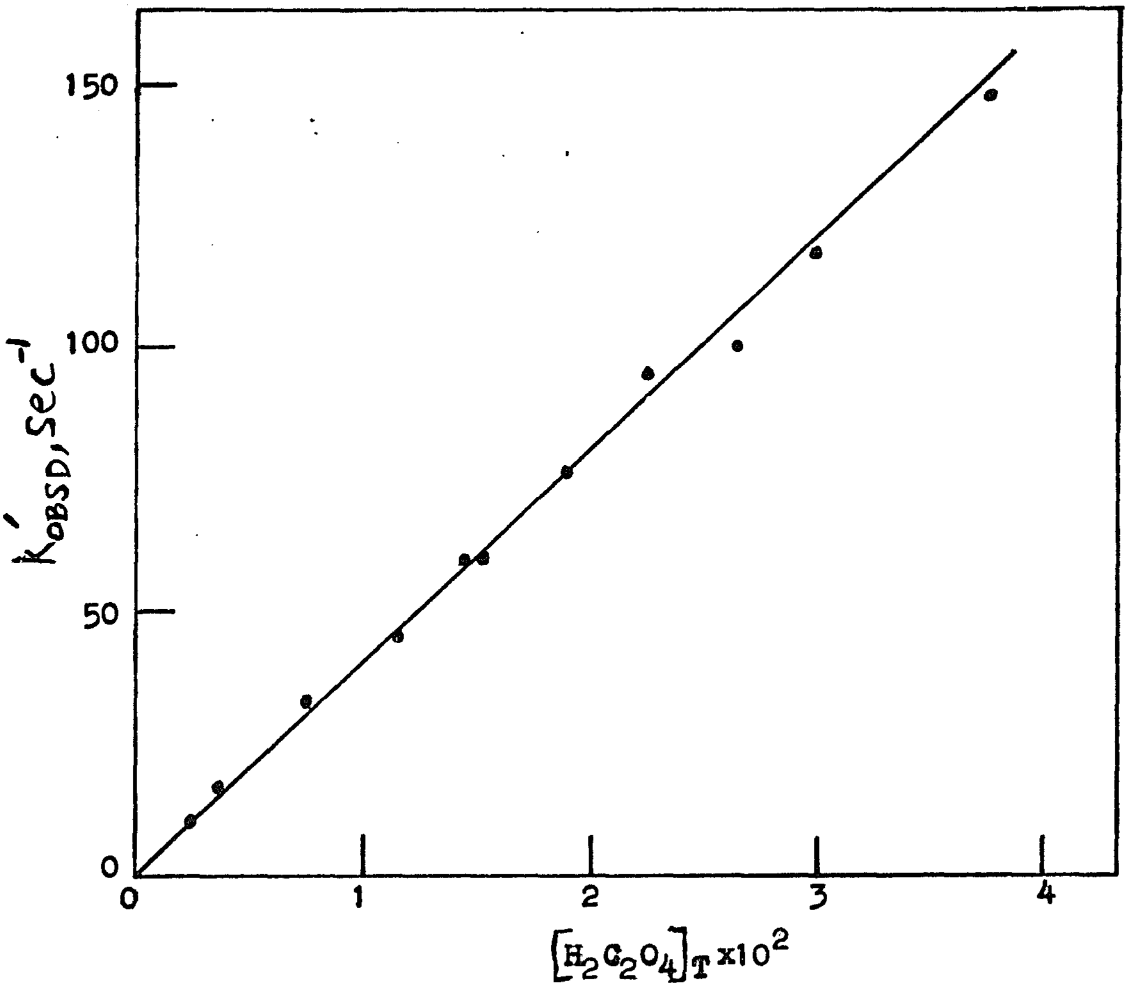

Fig. 14 Plot of k'_{OBSD} vs. $[H_2C_2O_4]_T$

This graph is based on the data in Table (XVII). The equation for the straight line, calculated by the method of least - squares, is $k'_{OBSD} = 3.90 \times 10^3 [H_2C_2O_4]_T$.

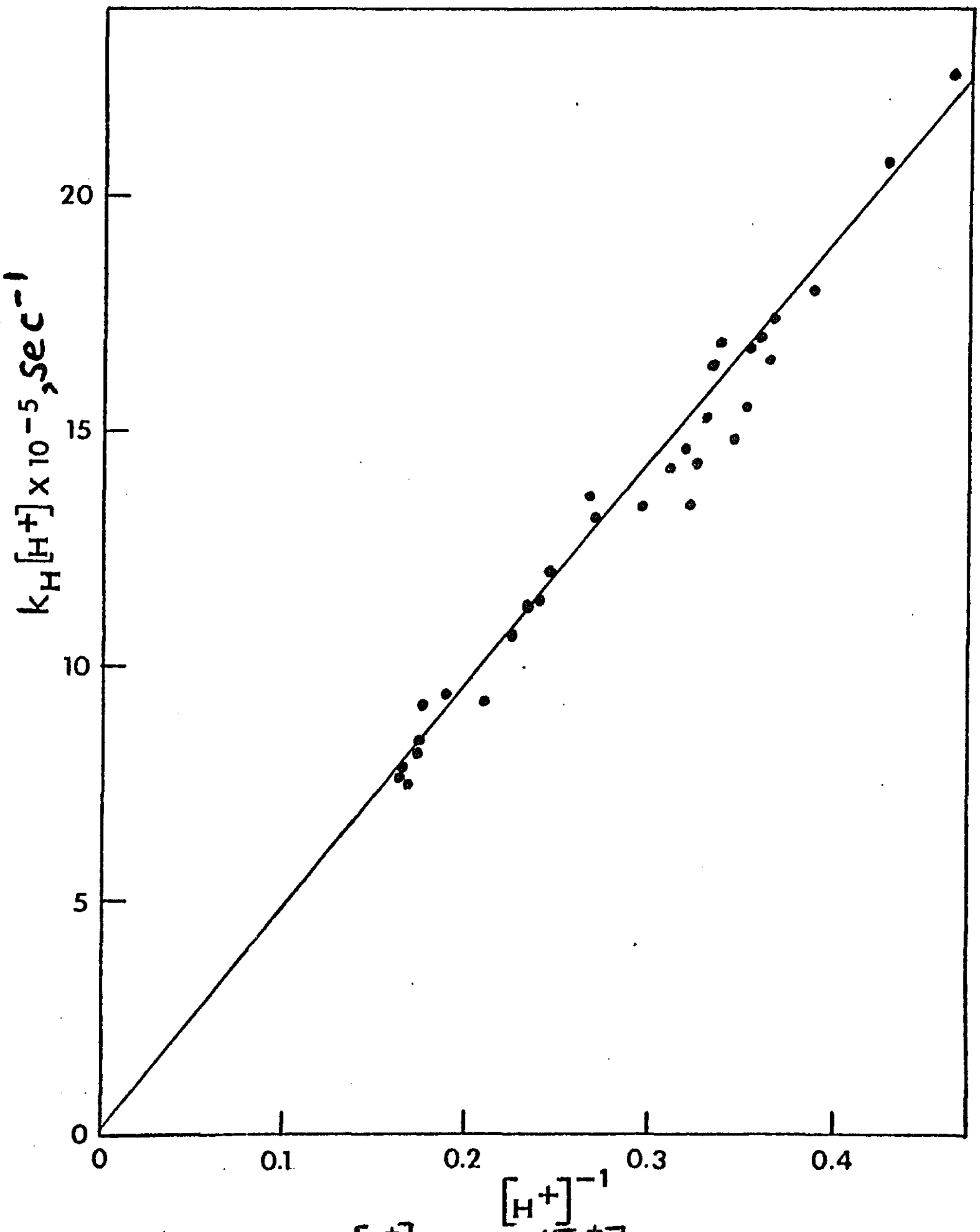

Fig.15 Plot of $k_H[H^+]$ vs. $1/[H^+]$

This graph is based on the data in Table(XVIII). The equation for the straight line, calculated by the method of least - squares, is $k_H[H^+] = 4.65 \times 10^6 / [H^+] + 1.22 \times 10^4$.

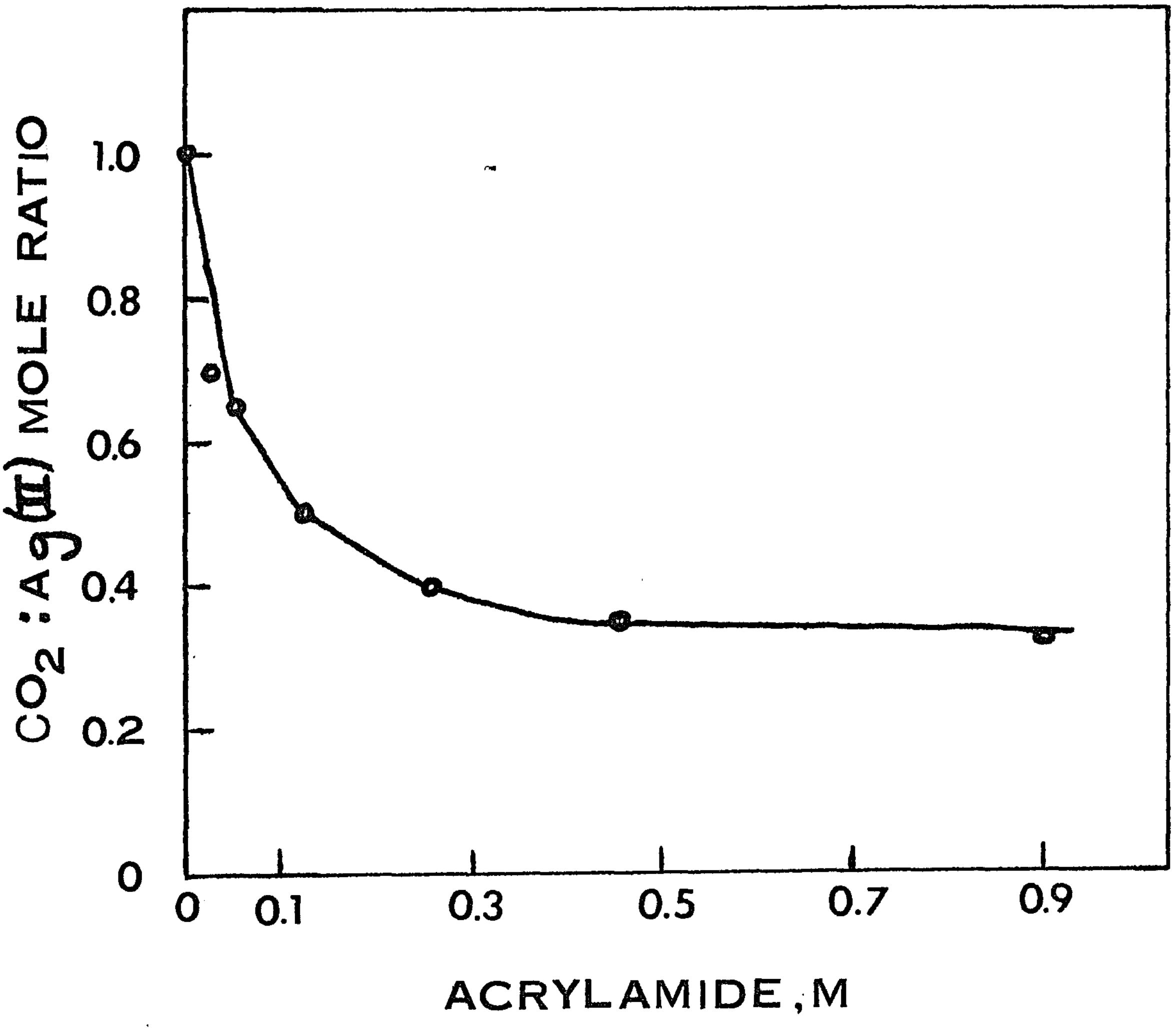

Fig. 16 Effect of Acrylamide on the CO_2:Ag(II) Mole Ratio

$[H_2C_2O_4]_T = 0.450$ M, $[Ag(II)] = 2.4\times10^{-2}$ M, $[HNO_3] = 6.32$ M

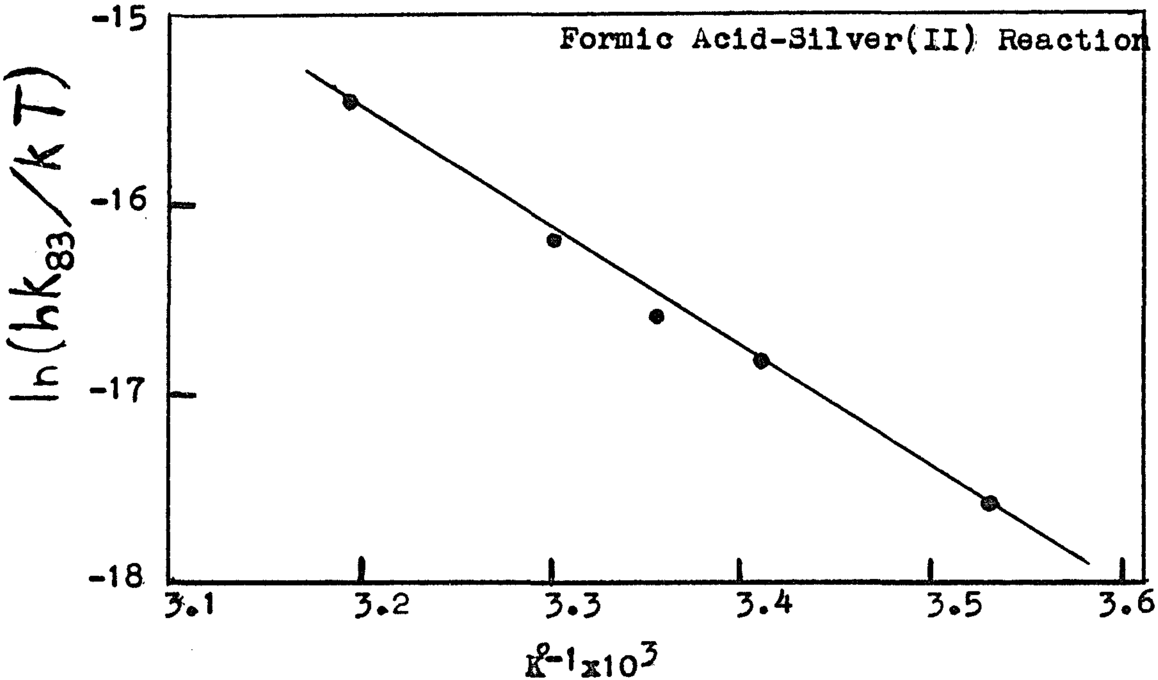

Fig. 17 Plot of ln (hk$_{83}$ / kT) vs. 1/°K

This graph is based on the data in Table(VII). The equation for the straight line, calculated by the method of least - squares, is ln (hk$_{83}$ / kT) = -6.21×10^3/°K + 4.32.

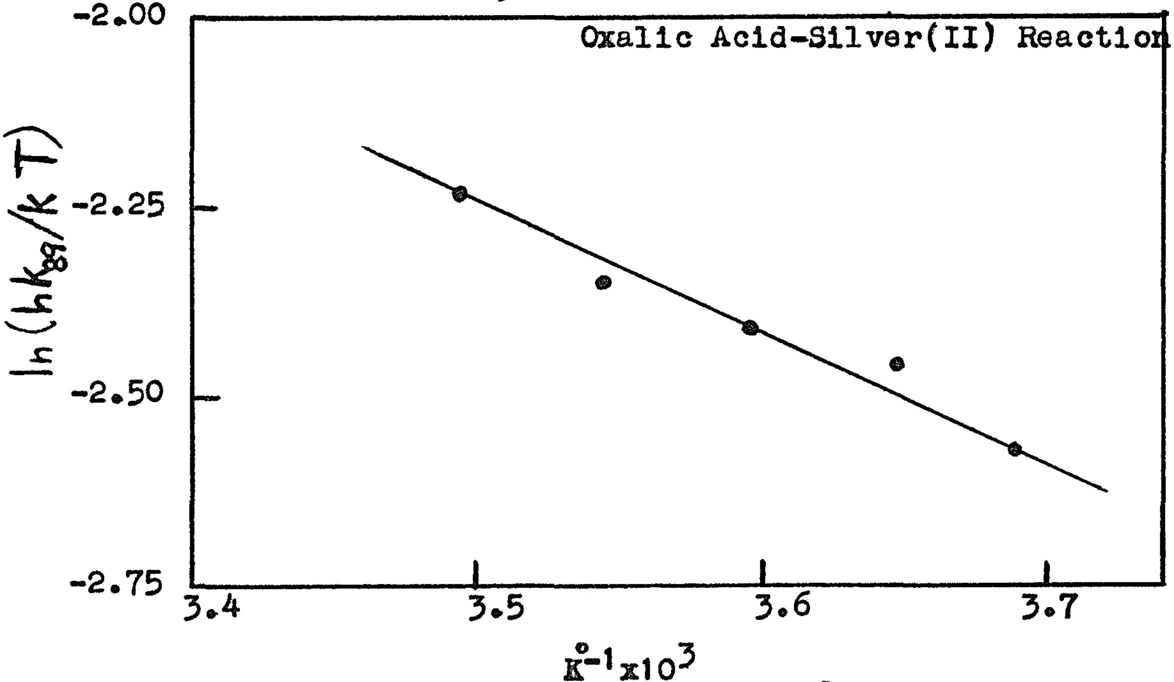

Fig. 18 Plot of ln (hk$_{89}$/ kT) vs. 1/°K

This graph is based on the data in Table(XX). The equation for the straight line, calculated by the method of least - squares, is ln (hk$_{89}$/ kT) = -1.6×10^3/°K + 3.5.

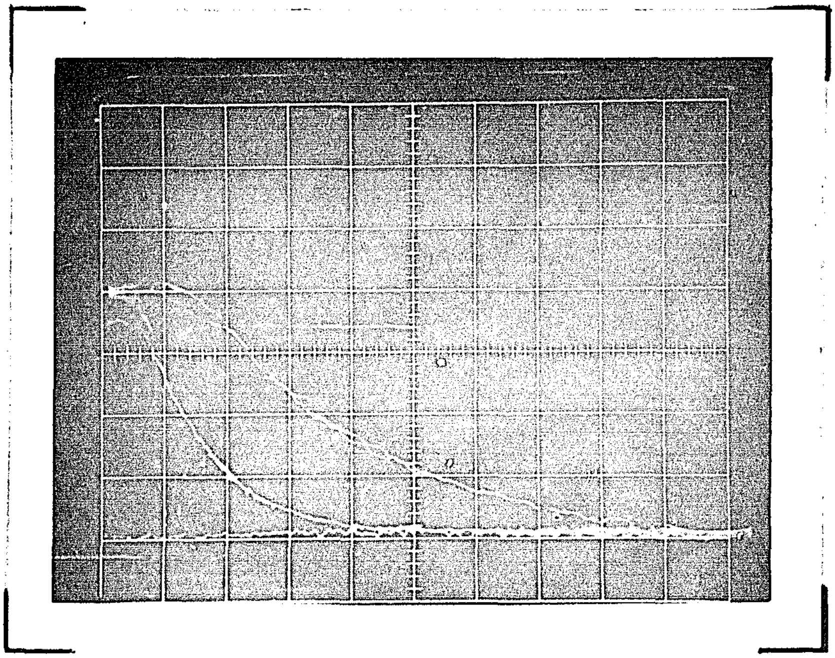

FIG. 19 TYPICAL KINETIC TRACES

Stopped - Flow conditions :

Absorbance/Div. (ordinate)	Time/Div. (abscissa)	Time Constant
0.04	2 msec 5 msec	0.1 msec

REACTANT A :

[Ag(II)] = 1.83×10^{-4} M
[Ag(I)] = 2.513×10^{-4} M
[HNO_3] = 5.997 M

REACTANT B :

[$H_2C_2O_4$]$_T$ = 12.07×10^{-4} M
[HNO_3] = 5.997 M

T = 5° C, λ = 365.0 nm, I = 6.00 M

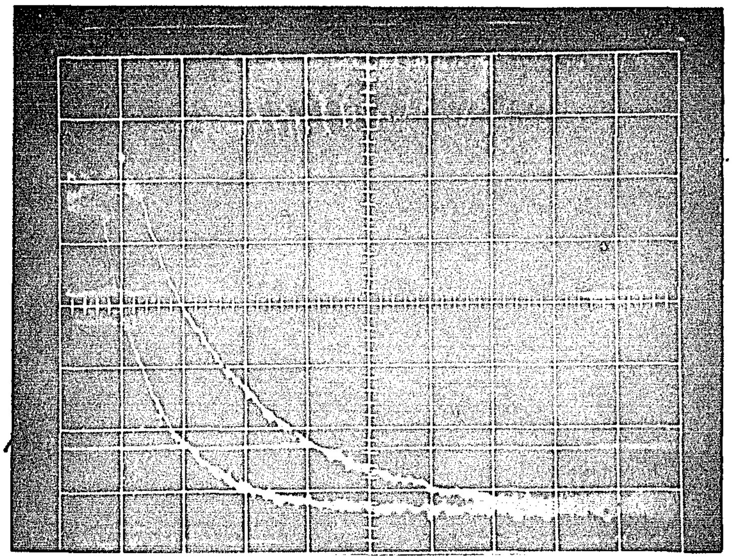

FIG. 20 TYPICAL KINETIC TRACES

Stopped - Flow conditions :

Absorbance/Div. (ordinate)	Time/Div. (abscissa)	Time Constant.
0.02	5 msec 10 msec	0.3 msec

REACTANT A:

$[Ag(II)] = 1.59\times10^{-4}$ M
$[HClO_4] = 4.000$ M
$[HNO_3] = 2.000$ M

REACTANT B :

$[H_2C_2O_4]_T = 12.06\times10^{-4}$ M
$[HClO_4] = 4.000$ M
$[HNO_3] = 2.000$ M

T = 5° C, λ = 365.0 nm, I = 6.00 M

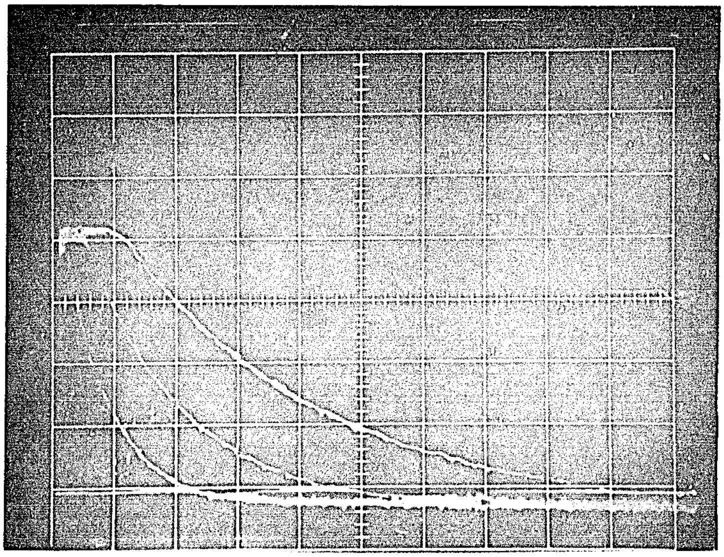

FIG. 21 TYPICAL KINETIC TRACES

Stopped - Flow conditions :

Absorbance/Div. (ordinate)	Time/Div. (abscissa)	Time Constant
0.02	5 msec 10 msec 20 msec	0.5 msec

REACTANT A :

$[\mathrm{Ag(II)}] = 1.04\times10^{-4}$ M
$[\mathrm{NaNO_3}] = 0.300$ M
$[\mathrm{HNO_3}] = 5.728$ M

REACTANT B :

$[\mathrm{H_2C_2O_4}]_T = 4.129\times10^{-4}$
$[\mathrm{NaNO_3}] = 0.300$ M
$[\mathrm{HNO_3}] = 5.728$ M

T = 5° C, λ=365.0 nm, I = 6.03 M

MECHANISM AND DISCUSSION

I. THE FORMIC ACID - SILVER(II)

A mechanism consistent with our results is

$$Ag^{2+} + HCO_2^- \rightleftharpoons AgHCO_2^+ \qquad K_{77}, \text{fast} \quad (77)$$

$$AgHCO_2^+ \longrightarrow Ag^+ + HCO_2\cdot \qquad k_{78}, \text{r.d.s} \quad (78)$$

$$Ag^{2+} + HCO_2\cdot \longrightarrow Ag^+ + CO_2 + H^+ \qquad k_{79}, \text{fast} \quad (79)$$

where step 78 is the rate determining step (r.d.s). Two equilibria also involved in this reaction are the ionization of formic acid in aqueous solution,

$$HCO_2H \rightleftharpoons HCO_2^- + H^+ \qquad K_{80} \quad (80)$$

and the silver(II) complexation with the nitrate ion,

$$Ag^{2+} + NO_3^- \rightleftharpoons AgNO_3^+ \qquad K_1 . \quad (1)$$

Appropriate combination of the above steps plus the use of the steady-state assumption yields the following rate law.*

$$-\tfrac{1}{2}\, d[Ag(II)]/dt = \frac{k_{78}\, K_{77}\, K_{80}\, [Ag(II)]\, [HCO_2H]_T}{\left\{1 + K_1\, [NO_3^-] + \dfrac{K_{77}\, K_{80}\, [HCO_2H]_T}{[H^+]}\right\}[H^+]} \qquad \text{(XIII)}$$

The term $[HCO_2H]_T$ ($= [HCO_2H] + [HCO_2^-]$) represents the total formic acid concentration. The total silver(II) concentration, $[Ag(II)]$, is given by

$$[Ag(II)] = [Ag^{2+}] + [AgNO_3^+] + [AgHCO_2^+]. \qquad \text{(XIV)}$$

The participation of silver(III) has been ruled out by the fact that silver(I) had no measurable effect on the observed rate constant.[48] If K_{77} is less than about $10^4\ M^{-1}$ then the $\left\{\dfrac{K_{77}\, K_{80}\, [HCO_2H]_T}{[H^+]}\right\}$ term (equation XIII term) $\ll$ than $(1 + K_1\, [NO_3^-])$

---

* Appendix I-A

term and can be neglected. The literature values for K_1 and K_{80} are $0.94 M^{-1}$ [13] and $1.77 \times 10^{-4} M$ [135] respectively, making the previous inequality reasonable. Equation (XIII) then simplifies to the observed rate law (XV), which predicts all the dependencies previously noted and found.

$$-\tfrac{1}{2}\, d\,[Ag(II)]/dt = \frac{k_{78}\, K_{77}\, K_{80}\, [Ag(II)]\,[HCO_2H]_T}{\{1 + K_1\,[NO_3^-]\}\,[H^+]} \qquad (XV)$$

One may now deduce that k_{OBSD} defined by equation (I) is

$$k_{OBSD} = \frac{2\, k_{78}\, K_{77}\, K_{80}\, [HCO_2H]_T}{\{1 + K_1\,[NO_3^-]\}\,[H^+]} \qquad (XVI)$$

and

$$k_{H,N} = \frac{2\, k_{78}\, K_{77}\, K_{80}}{\{1 + K_1\,[NO_3^-]\}\,[H^+]} = \frac{k_{OBSD}}{[HCO_2H]_T}\,. \qquad (XVII)$$

Also, at constant nitrate ion concentration the proportionality constant A from equation (III) is

$$A = \frac{2\, k_{78}\, K_{77}\, K_{80}}{\{1 + K_1\,[NO_3^-]\}} \qquad (XVIII)$$

while at constant acidity

$$B = \frac{2\, k_{78}\, K_{77}\, K_{80}}{[H^+]} \qquad (XIX)$$

and $K = K_1$. It is impossible to separate out the value of k_{78} and K_{77} from equation (XVIII), only the product of the two terms is attainable. The experimental value of $k_{78}\, K_{77}$ was found to be $3.9 \pm 0.3 \times 10^5\ M^{-1} sec.^{-1}$

It is possible to conceive of other mechanisms that give identical mathematical forms for the rate law. The following equilibrium 81, for example, may be important.

$$Ag^{2+} + HCO_2H \rightleftharpoons AgHCO_2^{+} + H^{+} \qquad (81)$$

It is however, kinetically indistinguishable from reactions 77 and 80 . If the $AgHCO_2^{+}$ complex intermediate then reacts via steps 78 and 79 the derived rate law (if equilibrium 81 was involved) would be

$$-\tfrac{1}{2}\, d[Ag(II)] / dt = \frac{k_{78}\, K_{81}\, [Ag(II)]\, [HCO_2H]_T}{\{1 + K_1\, [NO_3^-]\}\, [H^+]} , \qquad (XX)$$

where the value of $K_{77}\, K_{80}$ equals K_{81}. Similarly, one can conceive of other reaction pathways involving the formation of coordinated formic acid,

$$Ag^{2+} + HCO_2H \rightleftharpoons AgHCO_2H^{2+} \qquad (82)$$

followed by the electron transfer step has not been considered as significant due to the lack of a hydrogen ion independent term in the rate expression. If this equilibrium was important the form of equation (III) would have to be

$$k_{H,N} = A / [H^+] + C . \qquad (XXI)$$

Where C is a constant greater than zero (i.e. positive intercept for the plot of $k_{H,N}$ versus $1 / [H^+]$). Evidence for a C term in equation (III) was not observed.

An alternate two step mechanism can be proposed which does not involve the formation of an intermediate silver(II) -formate ion complex:

$$Ag^{2+} + HCO_2^{-} \longrightarrow Ag^{+} + HCO_2^{\circ} \qquad k_{83}, \text{r.d.s.} \; (83)$$

$$Ag^{2+} + HCO_2^{\circ} \longrightarrow Ag^{+} + CO_2 + H^{+} \qquad k_{84}, \text{fast} \; (84)$$

suitable combination of reactions 83 and 84 plus the equilibria in reactions 80 and 1 result in the following rate law.

$$-\tfrac{1}{2}\, d\left[Ag(II)\right] / dt = \frac{k_{83}\, K_{80}\, \left[Ag(II)\right] \left[HCO_2H\right]_T}{\left\{1 + K_1 \left[NO_3^-\right]\right\}\left[H^+\right]} \qquad (XXII)$$

Equation (XXII) is identical in form to equation (XV) derived for the first mechanism. The value of k_{83} can be determined and is found to have the same value as the $k_{78}\, K_{77}$ term previously discussed. Had the $\left\{\frac{K_{77}\, K_{80}\, \left[HCO_2H\right]_T}{\left[H^+\right]}\right\}$ term not been negligible in equation (XIII) the resulting rate expression for the two reaction pathways would have been different, as was found in other studies.[77,78,81] In an attempt to increase the importance of the $\left\{\frac{K_{77}\, K_{80}\, \left[HCO_2H\right]_T}{\left[H^+\right]}\right\}$ term the reaction was rerun at 10° C and the $\left[HCO_2H\right]_T$ was varied from 0.048M to 4.8M in 1.0M nitric acid solution at a constant ionic strength of 6.3M maintained using sodium perchlorate. (Table(VIII)) The reaction remained strictly first-order in formic acid throughout the entire range indicating that the $\left\{\frac{K_{77}\, K_{80}\, \left[HCO_2H\right]_T}{\left[H^+\right]}\right\}$ term remained negligible.

It is noteworthy that it is possible to conceive of a mechanism involving undissociated formic acid as the reactive species with Ag^{2+}. The following equilibrium would have to be considered, $HCO_2H + H^+ \rightleftharpoons HCO_2H_2^+$.

A mechanism that does not involve the formation of a free radical intermediate is given in steps 85 and 86.

$$Ag^{2+} + HCO_2^- \rightleftharpoons AgHCO_2^+ \qquad k_{85}, k_{-85} \quad (85)$$

$$Ag^{2+} + AgHCO_2^+ \longrightarrow 2Ag^+ + CO_2 + H^+ \qquad k_{86} \quad (86)$$

If one assumes that $k_{86} \gg k_{-85}$ the form of the derived rate law is identical to that in equation (XV) . As will be shown, the reaction pathway necessarily involves the formation of a free radical intermediate. Hence, this information eliminates the aforementioned mechanism as reasonable.

Kustin _et al._[13] have established that the silver(II) ion in nitric acid media consists primarily of the Ag^{2+} and $AgNO_3^+$ species. In perchloric acid solution the $AgOH^+$ species has been indicated as important. The value of K_1 (i.e. for equilibrium 1) which was obtained in this study is $3.8 \pm 0.7\ M^{-1}$ whereas the previously reported value is $\sim 0.94\ M^{-1}$.[13] A four fold difference between equilibrium values is not uncommon nor unreasonable. For example, Baker, Newton and Kahn[136] have obtained a value of $K \approx 12M$, for the first hydrolysis constant of cerium (IV), while Offner and Skoog[137] found that $K \approx 0.2M$. This represents a sixty fold difference in reported equilibrium constants for the same reaction.

It is noteworthy that intermediate metal ion-formate ion complexes similar to that presented in this work have been previously proposed for Mn(III),[77,78] Ce(IV)[81,82] and Cr(VI).[83] Additionally, evidence for the existence of metal ion-formic acid complexes has also been reported.[74,77,78,82]

The inhibitory effect of the nitrate ion is attributed to its competition with the formate ion for a coordination site on the aquometal cation Ag^{2+} ; therefore, as the nitrate ion concentration increases the actual concentration of $AgHCO_2^+$ decreases and the observed rate of reaction decreases. The inhibitory effect of the nitrate ion also precludes consideration of the $NO_3\cdot$ free radical species as a possible reactive intermediate in the reaction pathway.[47] It is interesting that where the nitrate ion was found to participate in other reactions it had an enhancing effect rather than an inhibiting effect.[47]

Thompson and Sullivan[85] have reported that the oxidation of formic acid by neptunium(VII) proceeds at a rate more rapid than that of any analogous system studied (note: up to 1972). These researchers indicated that this fact was consistent with the idea that an increase in oxidation potential of the metal ion couple necessarily meant an increase in the reaction rate. The Np(VII)/Np(VI) couple is ~2.0V[138] in aqueous perchloric acid. A comparison of the rate constants for the formic acid - neptunium(VII) reaction to those for the formic acid - silver(II) reaction indicate that the latter reaction is considerably faster. This means that a simple correlation between the rate constant and the oxidation potential of a metal ion species, for the oxidation of formic acid, is not generally possible.

Attempts to monitor any free radical species produced in the reaction using continuous flow techniques in conjunction with the e.s.r. spectrometer were unsuccessful. Reasons for this failure to detect a free radical species via e.s.r. techniques will be discussed later. A series of experiments were conducted which indicated that a free radical species was produced in the reaction. Acrylamide, a free radical scavenger, was used to detect the presence of free radical intermediates. The experiments undertaken to determine the stoichiometry via the Gas Buret Analyzer Apparatus were repeated except that now acrylamide was added to the formic acid solutions. In the presence of acrylamide the mole ratio of CO_2 : Ag(II) should decrease if a free radical species, such as HCO_2° , is present.[115,116] The results in Table (IX) confirm the presence of a free radical intermediate. The data is plotted in Fig. (7).

A study of the ionic strength effect (Table (X)) on this reaction is not conclusive but is indicative, since the concentrations used were far outside the range considered by the Debye - Hückel limiting law.[139] For a three fold change in the ionic strength there is a comparative small change in the observed rate constant (which may be caused by other medium effects). As the ionic strength increases the observed rate of reaction increases. This indicates that the reactive species may be characterized as an ion and a neutral molecule or two molecules which have formed a polar intermediate.[140]

II. THE OXALIC ACID - SILVER(II)

For clarity of presentation, the rate determining steps (r.d.s.) of a mechanism consistent with the results are presented (i.e. steps 87, 88, 89 and 90). The detailed mechanism and mathematical treatment are given in Appendix I-B

$$Ag^{2+} + HC_2O_4^- \longrightarrow Ag^+ + HC_2O_4^{\cdot} \qquad k_{87}, \text{r.d.s.} \qquad (87)$$

$$AgNO_3^+ + HC_2O_4^- \longrightarrow Ag^+ + HC_2O_4^{\cdot} + NO_3^- \qquad k_{88}, \text{r.d.s.} \qquad (88)$$

$$Ag^{2+} + C_2O_4^{2-} \longrightarrow Ag^+ + C_2O_4^{\cdot -} \qquad k_{89}, \text{r.d.s.} \qquad (89)$$

$$AgNO_3^+ + C_2O_4^{2-} \longrightarrow Ag^+ + C_2O_4^{\cdot -} + NO_3^- \qquad k_{90}, \text{r.d.s.} \qquad (90)$$

The binoxalate radical species, $HC_2O_4^{\cdot}$, and the oxalate radical ion, $C_2O_4^{\cdot -}$, produced react with silver(II) to form the reaction products. The following equilibria are also involved in the reaction mechanism.

$$H_2C_2O_4 \rightleftharpoons HC_2O_4^- + H^+ \qquad K_{95} \qquad (95)$$

$$HC_2O_4^- \rightleftharpoons C_2O_4^{2-} + H^+ \qquad K_{96} \qquad (96)$$

Appropriate combination of the reaction steps (Appendix I-B) including equilibria 95 and 96 yield the following rate law.

$$-\tfrac{1}{2}\, d\left[Ag(II)\right] / dt = \left\{\frac{k_{89}\ K_{95}}{[H^+]} + \frac{k_{89}\ K_{95}\ K_{96}}{[H^+]^2}\right\}\left[Ag(II)\right]\left[H_2C_2O_4\right]_T \qquad (XXIII)$$

This rate law predicts all the dependencies previously noted and found. The term $[H_2C_2O_4]_T$ ($=[H_2C_2O_4]+[HC_2O_4^-]+[C_2O_4{}^{2-}]$) represents the total oxalic acid concentration. The total silver(II) concentration, $[Ag(II)]$, in nitric acid solution is expressed in equation (XXIV).

$$\left[Ag(II)\right] = \left[Ag^{2+}\right] + \left[AgNO_3{}^+\right] \qquad (XXIV)$$

Additional silver(II) species, such as silver(II)-oxalate complex ion intermediates, have been omitted since this would predict a nitrate ion dependency which was not found. In the mechanism presented Ag^{2+} and $AgNO_3{}^+$ have similar, if not identical, reactivities. This is reasonable and expected if the reaction is diffusion controlled[141] (i.e. a product is formed as a result of each collision), with respect to both silver(II) species. This would also imply that the rate constants would be independent of the nitrate ion concentration, as was found. The participation of silver(III) has been ruled out by the fact that silver(I) has no measurable effect on the rate constant. (Table (XV))

It may now be seen that k'_{OBSD} , defined by equation (VI) is

$$k'_{OBSD} = 2 \left\{ \frac{k_{87}\ K_{95}}{[H^+]} + \frac{k_{89}\ K_{95}\ K_{96}}{[H^+]^2} \right\} [H_2C_2O_4]_T \ . \qquad (XXV)$$

The value of k_H , a second-order rate constant, is given by equation (XXVI).

$$k_H = 2 \left\{ \frac{k_{87}\ K_{95}}{[H^+]} + \frac{k_{89} K_{95}\ K_{96}}{[H^+]^2} \right\} = \frac{k'_{OBSD}}{[H_2C_2O_4]_T} \qquad (XXVI)$$

The constants k' and k'' presented in equation (XI) were found to have the following values (see Fig.(15)).

$$k' = 2\ k_{87}\ K_{95} = 1.22 \times 10^4 \ sec^{-1} \qquad (XXVII)$$

$$k'' = 2\ k_{89}\ K_{95}\ K_{96} = 4.65 \times 10^6 \ M\ sec^{-1} \qquad (XXVIII)$$

Darken's value for $K_{95} \left(= \frac{[H^+][HC_2O_4^-]}{[H_2C_2O_4]} \right)$ is 0.054M and Harned and Fallon's value for $K_{96} \left(= \frac{[H^+][C_2O_4^{2-}]}{[HC_2O_4^-]} \right)$ is 5.8×10^{-5}M at 25° C and 5° C, respectively.[142,143] The calculated value of k_{87} is $1.2 \pm 0.3 \times 10^5\ M^{-1} sec^{-1}$ and the value of k_{89} is $5.3 \pm 2.7 \times 10^{11}\ M^{-1} sec^{-1}$. These values were calculated using the values for K_{95} and K_{96} determined experimentally(Appendix IV). (The values presented will be discussed in the General Discussion Section).

The mechanism presented is most consistent with all the data. The magnitude of the rate constant k_{89} and the low heat of activation are indicative of a diffusion controlled reaction pathway.[141]

It is difficult to conceive of any mechanistic scheme for the reaction which would be kinetically indistinguishable. If one considered the $AgOH^{+}$ species in the reaction pathway a nitrate ion dependence would be found in the derived rate law. If one considered an equilibrium between Ag^{2+} and $AgNO_3^{+}$ with the appropriate oxalic acid species, again a nitrate ion dependence would be observed in the derived rate law, however, as previously mentioned, no nitrate ion effect was found experimentally.

The complex acidity dependence given in equation (XI) indicates that the reactive oxalic acid species are the binoxalate ion, $HC_2O_4^{-}$, and the oxalate dianion, $C_2O_4^{2-}$. It should be noted that equation (XI) may actually have the form,

$$k_H = k + \frac{k'}{[H^+]} + \frac{k''}{[H^+]^2} \quad . \qquad \text{(XXIX)}$$

There is no way to determine if k is significant from graphical methods.

Various attempts to detect any free radical intermediate(s) produced in this reaction using continuous flow techniques in conjunction with the e.s.r. spectrometer were unsuccessful. However, acrylamide was used to detect the presence of the free radical species produced in the 'slow' steps 87, 88, 89 and 90. As is shown in Appendix I-B these free radicals are consumed in steps 91,92,93 and 94.

As was found in the formic acid - silver(II) reaction the mole ratio of CO_2 : Ag(II) decreased significantly in the presence of acrylamide. The data is presented in Table(XXI) and plotted in Fig. (16) . This information is supportative of a free radical reaction pathway.

The ionic strengths used in this kinetic investigation were far outside the Debye - Hückel limiting law. As the ionic strength increases the observed rate of reaction decreases. The results of the ionic strength study are again indicative, rather than conclusive, that the reactive species are of opposite charges. (Table (XXII))

GENERAL DISCUSSION

The oxidation of organic substrates by silver(II) has been neglected by all but one group of researchers.[42] The mechanism for the oxidation of two carboxylic acids by silver(II) has been presented in this thesis. It is the intent of this section to make a comparison of the reaction pathways studied, noting similarities and differences. This section will also attempt to provide justifications for some of the mechanistic interpretations presented in this thesis.

Similarities: Formic acid reacted with the Ag^{2+} species and oxalic acid reacted with both the Ag^{2+} and $AgNO_3^+$ species, in neither study was there evidence to show that $AgOH^+$ or silver(III) participated in the reaction scheme. It is interesting to point out that although the Ag^{2+} ion and the $AgNO_3^+$ ion have different net charges their oxidation potentials are almost identical.[12,40] It was found that the reaction mechanism for both organic acids proceeded via two one-electron transfer steps to yield carbon dioxide and silver(I). It is noteworthy that the values for the rate constants for the reaction pathways involving the binoxalate ion species and the formate ion species are almost identical (i.e. 1.2×10^5 $M^{-1}sec^{-1}$ and 3.9×10^5 $M^{-1}sec^{-1}$, respectively). This indicates that these species have almost identical reactivities with silver(II). Unfortunately, the heat of activation could not be obtained for the reaction pathway involving the binoxalate ion species, nor could a possible nitrate ion dependence be detected because of the rapidity of the reaction of silver(II) with the oxalate dianion.

The effect of acrylamide, in both the formic acid and oxalic acid reactions with silver(II), proves that a free radical intermediate must have been produced. It should be noted that the mole ratio of CO_2 : Ag(II) levels off at a value other than zero in the presence of acrylamide(i.e. for the formic acid - silver(II) reaction the CO_2 : Ag(II) mole ratio levels off at about 0.2 and for the oxalic acid - silver(II) reaction at about 0.4). Hasan and Roček[115,116] found that the CO_2 : Cr(VI) ratio did not go to zero in the presence of acrylamide but were unable to explain this observation.

The e.s.r. experiments performed to detect the presence of a free radical intermediate(s) were unsuccessful because a). the steady state concentration of the free radical(s) species was below the detection limits of the e.s.r. apparatus or b). there was no free radical species present. However, the acrylamide experiments have ruled out the latter possibility. This is consistent with the proposed mechanisms. Differences: A significant difference in the oxidative pathways for the two carboxylic acids is the presence of a nitrate ion dependency in the formic acid - silver(II) reaction while this is not the case for the oxalic acid - silver(II) reaction. This is attributed to competition between the rate of complexation and the rate of electron transfer. In the case of the formic acid - silver(II) reaction complexation seems to be more rapid than the actual electron transfer process. Whereas, in the oxalic acid - silver(II) reaction the actual electron transfer process is much more rapid than any complexation reaction. It is significant to point out that the preponderance of reactions involving oxalic acid indicate that complexation in solution is common. If, for example, the oxalate dianion is involved in the reaction a stable five coordinate intermediate could be formed.

Additional insight as to why the electron transfer reaction is more rapid for oxalic acid than for formic acid with silver(II) may be seen from a comparison of their half-cell oxidation potentials.[144]

$$HCO_2H(aq.) \longrightarrow CO_2 + 2H^+ + 2e^- \qquad E_{\frac{1}{2}} = 0.20V \quad (97)$$

$$H_2C_2O_4(aq.) \longrightarrow 2CO_2 + 2H^+ + 2e^- \qquad E_{\frac{1}{2}} = 0.49V \quad (98)$$

On the basis of these half-cell potentials oxalic acid is thermodynamically favored over formic acid to be oxidized(via a two electron transfer step). However, this does not necessarily indicate that oxalic acid would have to be more rapidly oxidized than formic acid by other oxidants. The extreme rapidity of the oxalic acid - silver (II) reaction, compared to the formic acid - silver(II) reaction, is supported both by its large rate constants (see equations(XXVII) and (XXVIII)) and the low heat of activation (i.e. about three Kcal/mole) . A heat of activation around 2 - 3 Kcal/mole is usually indicative of a diffusion controlled reaction.[141]

It should be pointed out that the rate constant for the diffusion controlled reaction pathways, i.e. k_{89} and k_{90}, is at the high end of the typical diffusion controlled reaction (i.e. typically the second-order rate constants are in the range of about 10^9 to 10^{11}). This result may be explained if one considers that there are large instrumental errors in obtaining data for very fast reactions.[145] Also, if the equilibrium constants are in significant error this would contribute to the value for the rate constant. Eigen[146] has shown that there are reactions which may proceed more rapidly than a diffusion controlled reaction, namely by way of an electron 'tunnelling' effect (a non-classical electron jump through a potential barrier). As an illustration, Eigen discusses the reaction of the proton with the hydroxyl ion at 25°C and at ice temperature. The rate constant is $\sim 1.4 \times 10^{11} M^{-1} sec^{-1}$ at 25°C, however in ice the rate constant is $\sim 10^{13} M^{-1} sec^{-1}$. This latter value is significantly larger than classical theory on diffusion controlled reactions would allow.[147]

Further studies involving the silver(II) oxidation of other mono- and dicarboxylic acids (as well as other organic substrates) could a). investigate similarities and differences in mechanistic pathways and relative reactivities and b). attempt to develop a linear free energy relation(s) for a series of these reactions with different functional groups.

APPENDIX I-A

KINETIC EQUATIONS FOR THE FORMIC ACID-SILVER(II) REACTION

The loss of silver(II) can be represented as

$$-d\left[Ag(II)\right] / dt = k_{78}\left[AgHCO_2^+\right] + k_{79}\left[Ag^{2+}\right]\left[HCO_2\cdot\right] . \qquad (XXX)$$

This can be simplified, using reaction 77, to yield

$$-d\left[Ag(II)\right] / dt = k_{78}K_{77}\left[Ag^{2+}\right]\left[HCO_2^-\right] + k_{79}\left[Ag^{2+}\right]\left[HCO_2\cdot\right] \qquad (XXXI)$$

In order to solve for $HCO_2\cdot$ one may apply the steady-state assumption as follows,

$$-d\left[HCO_2\cdot\right] / dt = +d\left[HCO_2\cdot\right] / dt . \qquad (XXXII)$$

The loss of the formyl free radical with time is

$$-d\left[HCO_2\cdot\right] / dt = k_{79}\left[Ag^{2+}\right]\left[HCO_2\cdot\right] . \qquad (XXXIII)$$

The gain of the formyl free radical with time is

$$+d\left[HCO_2\cdot\right] / dt = k_{78}\left[AgHCO_2^+\right]. \qquad (XXXIV)$$

Setting equation (XXXII) equal to equation (XXXIV) results in a solution for the $\left[HCO_2\cdot\right]$.

$$\left[HCO_2\cdot\right] = \left(k_{78}\ K_{77} / k_{79}\right)\left[HCO_2^-\right] \qquad (XXXV)$$

Equation (XXXI) now simplifies to

$$-d\left[Ag(II)\right] / dt = 2k_{78}\ K_{77}\left[Ag^{2+}\right]\left[HCO_2^-\right] . \qquad (XXXVI)$$

Solving equation (XIV) in terms of $\left[Ag^{2+}\right]$ yields the following equation.

$$\left[Ag^{2+}\right] = \frac{\left[Ag(II)\right]}{\left\{1 + K_1\left[NO_3^-\right] + \dfrac{K_{77}\ K_{80}\left[HCO_2H\right]_T}{\left[H^+\right]}\right\}} \qquad (XXXVII)$$

Substituting equation (XXXVII) and the relationship in equation (XXXVIII),

$$\left[HCO_2^-\right] = K_{80}\left[HCO_2H\right]_T / \left[H^+\right], \qquad (XXXVIII)$$

into equation (XXXVI) yields the rate law given in equation (XIII). Equation (XIII) can be simplified to yield the observed rate law.

APPENDIX I-B

KINETIC EQUATIONS FOR

THE OXALIC ACID-SILVER(II) REACTION

The detailed mechanism for the reaction of oxalic acid with silver(II) is as follows,

$$Ag^{2+} + HC_2O_4^- \longrightarrow Ag^+ + HC_2O_4^{\circ} \qquad k_{87} \qquad (87)$$

$$AgNO_3^+ + HC_2O_4^- \longrightarrow Ag^+ + HC_2O_4^{\circ} + NO_3^- \qquad k_{88} \qquad (88)$$

$$Ag^{2+} + C_2O_4^{2-} \longrightarrow Ag^+ + C_2O_4^{-\circ} \qquad k_{89} \qquad (89)$$

$$AgNO_3^+ + C_2O_4^{2-} \longrightarrow Ag^+ + C_2O_4^{-\circ} + NO_3^- \qquad k_{90} \qquad (90)$$

$$Ag^{2+} + HC_2O_4^{\circ} \longrightarrow Ag^+ + 2CO_2 + H^+ \qquad k_{91} \qquad (91)$$

$$AgNO_3^+ + HC_2O_4^{\circ} \longrightarrow Ag^+ + 2CO_2 + NO_3^- + H^+ \qquad k_{92} \qquad (92)$$

$$Ag^{2+} + C_2O_4^{-\circ} \longrightarrow Ag^+ + 2CO_2 \qquad k_{93} \qquad (93)$$

$$AgNO_3^+ + C_2O_4^{-\circ} \longrightarrow Ag^+ + 2CO_2 + NO_3^- \qquad k_{94} \qquad (94)$$

Steps 87,88,89 and 90 are the rate determining steps. The loss of silver(II) can be represented as

$$-d[Ag(II)]/dt = k_{87}[Ag^{2+}][HC_2O_4^-] + k_{88}[AgNO_3^+][HC_2O_4^-] + k_{89}[Ag^{2+}][C_2O_4^{2-}] + k_{90}[AgNO_3^+][C_2O_4^{2-}] + k_{91}[Ag^{2+}][HC_2O_4^{\circ}] + k_{92}[AgNO_3^+][HC_2O_4^{\circ}] + k_{93}[Ag^{2+}][C_2O_4^{-\circ}] + k_{94}[AgNO_3^+][C_2O_4^{-\circ}] \; . \qquad (XXXIX)$$

In order to solve for $[HC_2O_4^{\circ}]$ and $[C_2O_4^{-\circ}]$ one may apply the steady-state approximation to these species, i.e.

$$-d[HC_2O_4^{\circ}]/dt = +d[HC_2O_4^{\circ}]/dt \text{ and} \qquad (XL)$$

$$-d[C_2O_4^{-\circ}]/dt = +d[C_2O_4^{-\circ}]/dt \; . \qquad (XLI)$$

The loss of $[HC_2O_4^{\circ}]$ can be expressed as

$$-d[HC_2O_4^{\circ}]/dt = k_{91}[Ag^{2+}][HC_2O_4^{\circ}] + k_{92}[AgNO_3^+][HC_2O_4^{\circ}] \qquad (XLII)$$

The gain of $[HC_2O_4^{\circ}]$ can be expressed as

$$+d[HC_2O_4^{\circ}]/dt = k_{87}[Ag^{2+}][HC_2O_4^-] + k_{88}[AgNO_3^+][HC_2O_4^-] \; . \qquad (XLIII)$$

Setting equation (XLII) equal to equation (XLIII) and solving for $[HC_2O_4^{\circ}]$ yields,

$$[HC_2O_4\cdot] = \frac{k_{87}[Ag^{2+}][HC_2O_4^-] + k_{88}[AgNO_3^+][HC_2O_4^-]}{k_{91}[Ag^{2+}] + k_{92}[AgNO_3^+]} \quad \text{(XLIV)}$$

Since there is no nitrate ion effect on the reaction rate the Ag^{2+} and $AgNO_3^+$ species must have the same reactivities with the appropriate oxalate species. It follows that $k_{87} = k_{88}$, $k_{89} = k_{90}$, $k_{91} = k_{92}$ and $k_{93} = k_{94}$. Equation (XLIV) may now be simplified to yield

$$[HC_2O_4\cdot] = (k_{87}/k_{91})[HC_2O_4^-]. \quad \text{(XLV)}$$

Similarly, the loss of $[C_2O_4^-\cdot]$ may be expressed as

$$-d[C_2O_4^-\cdot]/dt = k_{93}[Ag^{2+}][C_2O_4^-\cdot] + k_{94}[AgNO_3^+][C_2O_4^-\cdot] \quad \text{(XLVI)}$$

The gain of $[C_2O_4^-\cdot]$ can be expressed as

$$+d[C_2O_4^-\cdot]/dt = k_{89}[Ag^{2+}][C_2O_4^{2-}] + k_{90}[AgNO_3^+][C_2O_4^{2-}]. \quad \text{(XLVII)}$$

Setting equation (XLVI) equal to equation (XLVII) yields

$$[C_2O_4^-\cdot] = \frac{k_{89}[Ag^{2+}][C_2O_4^{2-}] + k_{90}[AgNO_3^+][C_2O_4^{2-}]}{k_{93}[Ag^{2+}] + k_{94}[AgNO_3^+]} \quad \text{(XLVIII)}$$

Equation (XLVIII) can be simplified, noting that $k_{89}=k_{90}$ and $k_{93}=k_{94}$, to yield

$$[C_2O_4^-\cdot] = (k_{89}/k_{93})[C_2O_4^{2-}]. \quad \text{(XLIX)}$$

The rate law in equation (XXXIX) may now be rewritten as follows,

$$\begin{aligned} -d[Ag(II)]/dt = {} & 2k_{87}[Ag^{2+}][HC_2O_4^-] + 2k_{87}[AgNO_3^+][HC_2O_4^-] \\ & + 2k_{89}[Ag^{2+}][C_2O_4^{2-}] + 2k_{89}[AgNO_3^+][C_2O_4^{2-}]. \end{aligned} \quad \text{(L)}$$

Substituting equation (LI), obtained from reaction 1,

$$[AgNO_3^+] = K_1[Ag^{2+}][NO_3^-] \quad \text{(LI)}$$

into the rate expression (L) yields the following equation.

$$\begin{aligned} -d[Ag(II)]/dt = {} & 2\{k_{87}[Ag^{2+}][HC_2O_4^-] + k_{89}[Ag^{2+}][C_2O_4^{2-}]\} \\ & x\ \{1 + K_1[NO_3^-]\} \end{aligned} \quad \text{(LII)}$$

The total silver(II) concentration, $[Ag(II)]$, from equation (XXIV) can be expressed in terms of $[Ag^{2+}]$.

$$[Ag^{2+}] = \frac{[Ag(II)]}{\{1 + K_1[NO_3^-]\}} \qquad \text{(LIII)}$$

Substituting equation (LIII) into the rate equation (LII) yields,

$$-d[Ag(II)]/dt = 2\{k_{87}[HC_2O_4^-] + k_{89}[C_2O_4^{2-}]\}Ag(II) \qquad \text{(LIV)}$$

The equilibria in reactions 95 and 96 can be used to solve for the $[HC_2O_4^-]$ and $[C_2O_4^{2-}]$ yielding

$$[HC_2O_4^-] = \frac{K_{95}[H_2C_2O_4]_T}{[H^+]} \qquad \text{(LV)}$$

and

$$[C_2O_4^{2-}] = \frac{K_{95}\,K_{96}[H_2C_2O_4]_T}{[H^+]^2} \ . \qquad \text{(LVI)}$$

Substituting the values for $HC_2O_4^-$ and $C_2O_4^{2-}$ into equation (LIV) yields the observed rate law (XXIII). The observed rate law indicates that the Ag^{2+} and $AgNO_3^+$ ions must have identical reactivities with the binoxalate ion and the oxalate dianion species.

APPENDIX II

DUAL BURET GAS ANALYSIS APPARATUS

A Dual Buret Gas Analyzer Apparatus[148], shown in Fig. (22), was used to determine the stoichiometry of the reactions studied. It allows one to mix the two reactants to any desired ratio and then to collect the carbon dioxide evolved at a known pressure and temperature in order to determine the number of moles of gas liberated. A weighed amount of silver (II) oxide on an aluminum pan is placed in flask A. The formic acid solution or oxalic acid solution (both run without and with acrylamide present) is contained in buret B. With stopcocks #3 and #4 open and stopcock #1 closed, helium was then allowed to flow through stopcock #2 into flask A and the entire system. This procedure purges the apparatus of air and replaces it with helium at atmospheric pressure. After purging, stopcock #4 was turned to permit the gas buret, G, to communicate with flask A and stopcocks #2 and #3 remained closed. The helium was then adjusted to atmospheric pressure by matching the heights of the liquid in the gas buret, G, and the leveling bulb, H. The contents of buret B were admitted into flask A through stopcock #1. If no carbon dioxide was evolved the volume of liquid entering flask A would displace an equivalent volume of gas back into buret B and the liquid level in the gas buret G would remain unchanged. The liquid level in buret G would change only if gas was evolved in the reaction. In this manner the volume of gas liberated at constant temperature and pressure was determined.

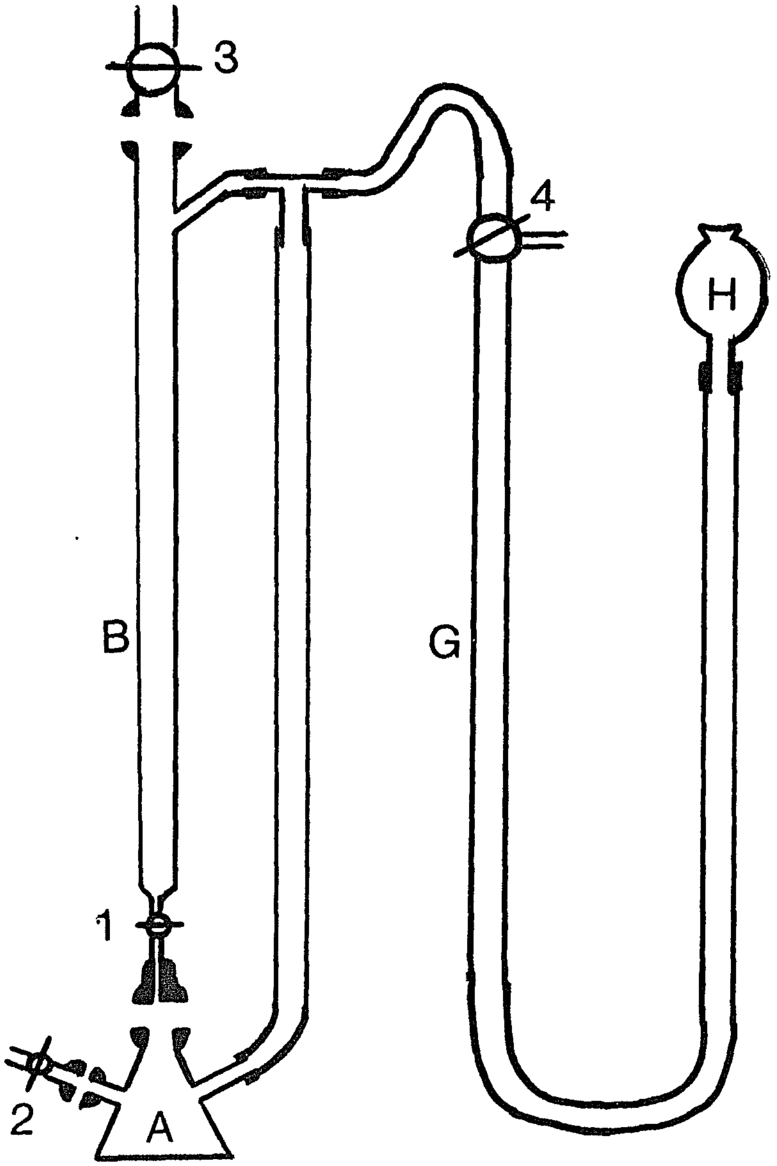

Fig.22 Dual Buret Gas Analysis Apparatus

APPENDIX III

DETERMINATION OF THERMODYNAMIC PARAMETERS

Analysis of the effect of temperature on the rate of reaction was made in terms of the Eyring equation.[149]

$$k_{OBSD} = (k\ T\ /\ h)\ \exp(\Delta S^{\ddagger}/\ R)\ \exp(-\Delta H^{\ddagger}/\ RT)\ ^{*} \qquad \text{(LVII)}$$

For the formic acid-silver(II) reaction and for the oxalic acid-silver(II) reaction the effect of temperature on k_{83} $(=k_{78}K_{77})$ and k_{89} were studied, respectively.

For the formic acid-silver(II) reaction plots of $k_{H,N}$ versus $1\ /[H^+]$ were determined at various temperatures. At each temperature a value for k_{83} was calculated.

$$k_{83} = (k\ T\ /\ h)\ \exp(\Delta S^{\ddagger}/\ R)\ \exp(-\Delta H^{\ddagger}/\ RT) \qquad \text{(LVIII)}$$

Equation (LVIII) can be rearranged to yield

$$\ln\left(\frac{k_{83}h}{k\ T}\right) = -\Delta H^{\ddagger}/\ RT + \Delta S^{\ddagger}/\ R \quad . \qquad \text{(LIX)}$$

A plot of $\ln(k_{83}\ h\ /\ kT)$ versus $(1\ /\ T)$ is linear with a slope of $-\Delta H^{\ddagger}/\ R$ and an intercept of $\Delta S^{\ddagger}/\ R$. (See Fig. 17).

Similarly, for the oxalic acid-silver(II) reaction plots of $k_H[H^+]$ versus $1\ /[H^+]$ were determined at various temperatures. At each temperature a value for k_{89} was calculated.

$$k_{89} = (k\ T\ /\ h)\ \exp(\Delta S^{\ddagger}/\ R)\exp(-\Delta H^{\ddagger}/\ RT) \qquad \text{(LX)}$$

Equation (LX) can be rearranged to yield a form identical to equation(LIX). A plot of $\ln\left(\frac{k_{89}\ h}{k\ T}\right)$ versus $(1\ /\ T)$ is linear with a slope of $-\Delta H^{\ddagger}/\ R$ and an intercept of $\Delta S^{\ddagger}/\ R$. (See Fig. 18). (note: $R = 1.987$ cal/ mole °K)

*$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the enthalpy of activation and the entropy of activation, respectively. The other symbols have their usual meanings.

APPENDIX IV

THE DETERMINATION OF THE EQUILIBRIUM CONSTANTS FOR OXALIC ACID

A method to calculate the ionization constants of dibasic acids from titration curves has been described by Noyes[150] and Britton.[151] The details of the complete derivation are contained in these papers, only the important equations and definition actually used will be presented.

A dibasic acid, namely oxalic acid, will be denoted as H_2R. The H_2R species ionizes in aqueous medium as follows.

$$H_2R \rightleftharpoons H^+ + HR^- \qquad K_{H_2R}$$

$$HR^- \rightleftharpoons H^+ + R^{2-} \qquad K_{HR}$$

Let $[C]$ = the total concentration of of oxalic acid being titrated

(note: $[C] = [H_2R] + [HR^-] + [R^{2-}]$)

Let $[B]$ = the total concentration of sodium hydroxide added

Let $[H^+]$ = the total concentration of hydrogen ions in solution (determined from pH measurements)

The following relationships are of importance:

Let $X_n = [B]_n[H^+]_n + [H^+]^2_n - [H^+]_n[C]_n$ (LXI)

Let $Y_n = 2[C]_n - [B]_n - [H^+]_n$ (LXII)

Let $Z_n = [H^+]^2([B]_n + [H^+]_n)$ (LXIII)

The subscript n refers to the data taken from specific points on the titration curve. Hence, by taking any pair of readings selected from opposite sides of the inflection point (or mid-point) of the titration curves whose parameters are X_1, Y_1, Z_1 and X_2, Y_2, Z_2, the values of K_{H_2R} and K_{HR} can be calculated using the following equations.

$$K_{H_2R} = (Y_1Z_2 - Y_2Z_1) / (X_1Y_2 - X_2Y_1) \qquad \text{(LXIV)}$$

$$K_{HR} = (X_1Z_2 - X_2Z_1) / (Y_1Z_2 - Y_2Z_1) \qquad \text{(LXV)}$$

The calculated values for the equilibrium constants are $K_{95} = 0.051 \pm 0.013M$ and $K_{96} = 8.2 \pm 4.1 \times 10^{-5}M$. The data is plotted in Fig.(23).

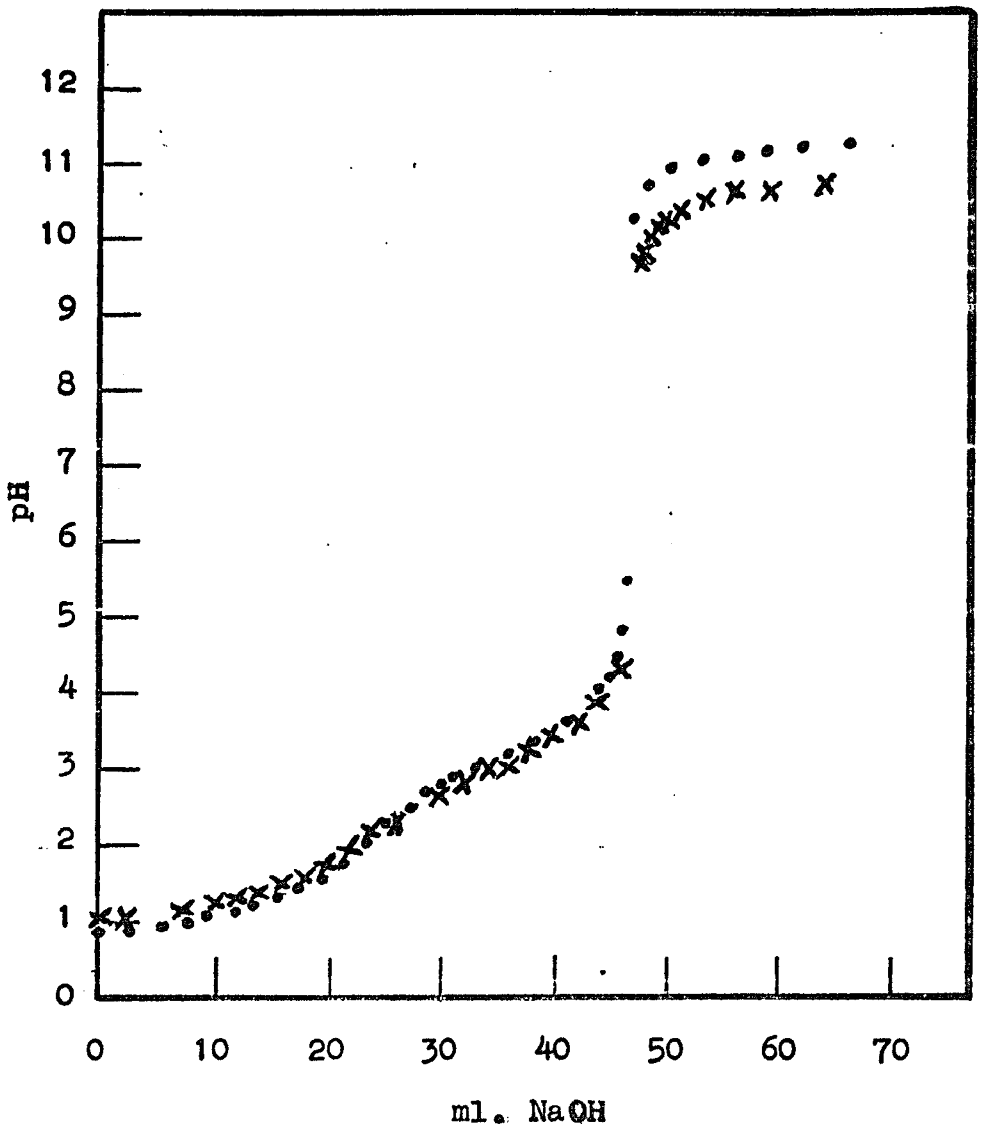

Fig. 23 Titration curve for oxalic acid. Titration of 100 ml. of 0.02550 M oxalic acid with 0.1073 N NaOH.

● data at 5°C

x data at 25° C

Note: The ionic strength for all determinations is 6.0 M.

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