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MALONIC ACID AND ITS DERIVATIVES.

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KINETIC STUDY OF THE SILVER (II) OXIDATION OF MALONIC ACID AND ITS DERIVATIVES

by

TOBY A. SCHEINBART

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

1978

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.

5/8/78 — Jack I. Morrow
date — Chairman of Examining Committee

5/15/78 — Leonard H. Schwartz
date — Executive Officer

Juan P. Villa

Irving Waltcher
Supervisory Committee

The City University of New York

ABSTRACT

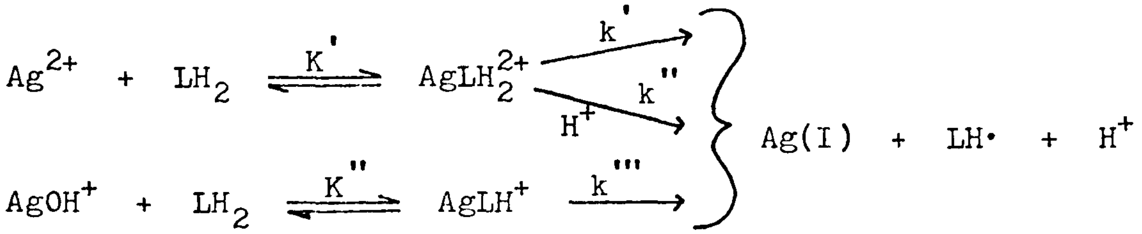
KINETIC STUDY OF THE SILVER (II) OXIDATION OF MALONIC ACID AND ITS DERIVATIVES

by

TOBY A. SCHEINBART

Mentor: Professor Jack I. Morrow

The kinetics and mechanism of the oxidation of malonic, methylmalonic, ethylmalonic, dimethylmalonic, and diethylmalonic acids in nitric acid media have been studied using the stopped-flow technique. The data are interpreted in terms of the following generalized reaction scheme:



where LH_2 represents malonic, methylmalonic, ethylmalonic, dimethylmalonic, and diethylmalonic acids.

For malonic acid, k' and k'' are important relative to k'''. For methyl- and ethylmalonic acids, k' and k''' are important relative to k''. For dimethyl- and diethylmalonic acids, k''' is important relative to k' and k''.

TO

MY FIANCE,

JOSEPH I. TROMPETER, M.D.

AND

TO

MY PARENTS,

IRVING AND SHIRLEY SCHEINBART

ACKNOWLEDGMENTS

Many heartfelt thanks are due
Professor Jack I. Morrow
for his guidance, patience,
understanding, and friendship.

I also wish to thank
the members of my thesis committee
for their cooperation.

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INTRODUCTION

Argentic ion in solution can be prepared in various ways. It is formed in the anodic oxidation of silver (I) salts[1] or by the treatment of silver (I) salts with potassium peroxysulfate[2], with ozone[3], or with fluorine[4]. Argentic ion in solution can also be prepared by adding solid AgO (Ag(I)-O-Ag(III)-O) to an acid solution.[5] Regardless of preparative method, the argentic compound has the same oxidizing power.

Noyes et. al[6] have proven that the argentic compound exists mainly as the bipositive ion in acid solution. Its magnetic moment is consistent with a d^9 system. Ag(III) ions do form through the bimolecular process:

$$2Ag(II) \rightleftharpoons Ag(III) + Ag(I) \qquad (1)$$

but they exist in insignificant amounts (~0.03%) since the equilibrium lies far to the left. Ag(II) represents all bipositive silver species which exist in acid solution.

The properties of Ag(II) in various acidic solvents have been studied by many workers.[7-10] Rechnitz and Zamochnick[7] found that in sulfuric acid, silver (II) forms two sulfato complexes. They did not report on the stoichiometry of the complexes but rather presented evidence for their existence. The first has an absorption maximum between 245 and 262 nm. and the second has an absorption maximum between 343 and 368 nm. The actual position of the maximum changes with acid concentration. The first complex predominates when $[H_2SO_4]$ is between four and nine molar, and the second complex dominates when $[H_2SO_4]$ is between 10 and 18 M. In 10 M H_2SO_4, the absorbances of the two complexes are equal. An isosbestic point, observed at 310 nm. when $[H_2SO_4] = 12$ or 18 M, confirmed the existence of these two complexes.

The ultra-violet and visible spectra of Ag(II) in phosphoric acid media show that at least two silver (II) - phosphato complexes, with absorption maxima at around 300 and 498 nm., are present in the concentration range of 4 - 44.4 N H_3PO_4.[8]

Kirwin and coworkers[9] have examined Ag(II) in perchloric acid media. The spectrum (shown in Figure 1) shows a maximum at 475 nm. which is attributed to an internal ligand field d ← d transition. The molar absorptivity is 1.4×10^2 $M^{-1}cm^{-1}$. In addition, there is a shoulder at 575 nm. and the tail of a charge transfer band starting at around 380 nm. and increasing into the ultra-violet. The intensity of the maximum at 475 nm. does not change with $[HClO_4]$ but its shape is slightly altered and there are large changes in the shoulder and charge transfer bands. Kirwin thought these changes were due to a Ag(II)-perchlorate complex but later attributed them to medium effects[10].

In nitrate media[10], the Ag(II) absorption maximum (shown in Figure 2) occurs around 390 nm and both the absorption coefficient and position of the maximum are $[NO_3^-]$ dependent. This peak is attributed to a Ag(II)-nitrato complex, $AgNO_3^+$, which forms according to the equilibrium:

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

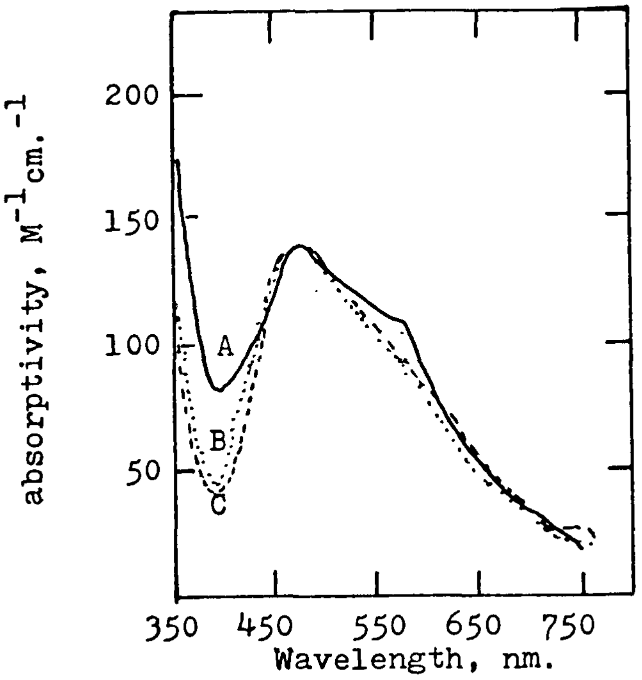


Figure 1.

Absorption Spectrum
of Ag(II)
in Perchloric Acid

A - 6.0 M $HClO_4$
B - 3.0 M $HClO_4$
C - 1.5 M $HClO_4$

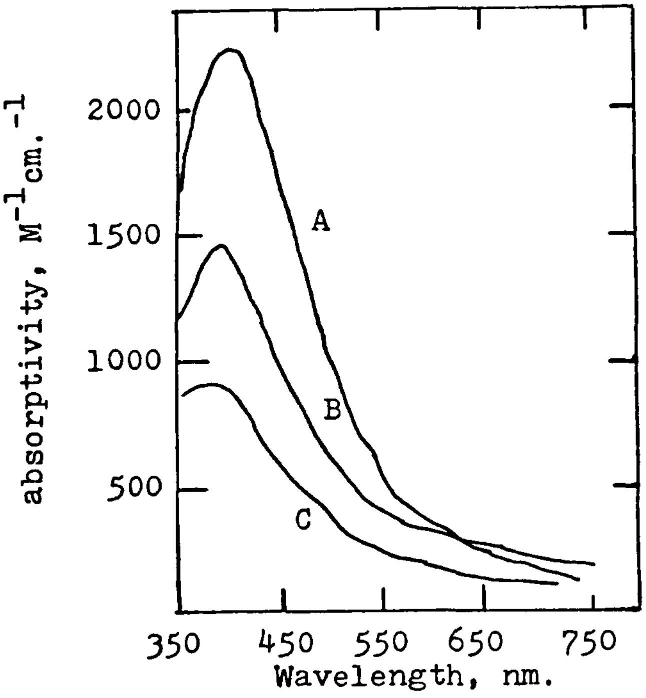


Figure 2.
Absorption Spectrum
of Ag(II)
in Nitric Acid

A - 6.0 M HNO_3
B - 3.0 M HNO_3
C - 1.5 M HNO_3

The equilibrium constant, K, for this reaction, given by

$$K = \frac{[AgNO_3^+]}{[Ag^{2+}][NO_3^-]} \tag{3}$$

is 0.91 M^{-1}. The absorption coefficient is acid dependent which is explained by the hydrolysis of Ag(II)

$$Ag^{2+} + H_2O \rightleftharpoons AgOH^+ + H^+. \tag{4}$$

The hydrolysis constant, K_H, given by

$$K_H = \frac{[AgOH^+][H^+]}{[Ag^{2+}]} \tag{5}$$

is 0.69 M.

So, in nitric acid media, three silver (II) species exist: the aquated ion, Ag^{2+}, the first hydrolysis product, $AgOH^+$, and the nitrato complex, $AgNO_3^+$, all of which are potential reactants.

It can be seen that silver (II) readily forms complexes with many ligands, such as SO_4^{2-}, PO_4^{3-}, and NO_3^-.

Silver (II) is one of the most powerful oxidizing reagents. The Ag(II)/Ag(I) couple is +1.93 V in 4 M nitric acid and 2.00 V in 4 M perchloric acid.[11] There are two general mechanistic paths for oxidation of a substrate, S, by silver (II). They are:

<u>Path 1</u>

$$2Ag(II) \rightleftharpoons Ag(I) + Ag(III) \tag{6}$$

$$Ag(III) + S \longrightarrow Ag(I) + S^{2+} \tag{7}$$

<u>Path 2</u>

$$Ag(II) + S \longrightarrow Ag(I) + S^+ \tag{8}$$

$$Ag(II) + S^+ \longrightarrow Ag(I) + S^{2+} \tag{9}$$

where S^{2+} may further react.

In Path 1, the substrate is oxidized in a one-step 2 electron transfer process whereas, in Path 2, two 1 electron steps are required. Not shown in these two pathways is the possibility of complexation prior to electron transfer. In Path 1, Ag(III) is the reactive silver species, its existence being reflected in the kinetic expression by the appearance of a $[Ag(II)]^2/[Ag(I)]$ term in the rate expression. For Path 2, the reactive silver species is the bipositive ion, which in nitrate media exists as Ag^{2+}, $AgOH^+$, and $AgNO_3^+$.

In reactions where oxidations occur via Path 2, the relative reactivity of the three Ag(II) species is of prime interest. A knowledge of which is the most reactive species provides a more intimate understanding of the redox process. Where Ag^{2+} is the reactive species, the reaction usually proceeds by an electron transfer. When $AgOH^+$ dominates, H atom transfer is usually occurring. In cases where NO_3^- catalyzes the reaction, $AgNO_3^+$ is the most reactive form.

The silver (I) - silver (II) exchange reaction in perchloric acid[12] was found to be 2nd order in Ag(II) and has a large inverse $[H^+]$ dependency which suggests that $AgOH^+$ is involved in the rate determining step.

The reduction of Ag(II) by water in various acidic solvents to produce oxygen and Ag(I) has been studied.[7,8,9,10] The overall reaction is

$$4Ag(II) + 2H_2O \longrightarrow 4Ag(I) + O_2 + 4H^+. \qquad (10)$$

When the solvent is sulfuric[7], phosphoric[8], or perchloric[9] acid, the rate law is second order with respect to Ag (II) and inverse order with respect to Ag(I). These oxidations occur by Path 1 with Ag(III) being formed and reacting with water to give products.

A similar mechanism is proposed when nitric acid is the solvent and $[Ag(II)] > 1 \times 10^{-4}$ M.[13] However, when $[Ag(II)] < 1 \times 10^{-4}$ M, the rate law is 1st order in Ag(II). These results show that oxidation can occur by both Path 1 and Path 2 simultaneously.

Silver (II) oxidizes phosphorous acid in perchloric acid media to phosphoric acid.[14] The overall reaction is

$$2Ag(II) + H_3PO_3 + H_2O \longrightarrow 2Ag(I) + H_3PO_4 + 2H^+. \tag{11}$$

The rate law, given by

$$\text{rate} = k_1[H_3PO_3] + \frac{k_2[Ag(II)]^2[H_3PO_3]}{[Ag(I)]}, \tag{12}$$

indicates two parallel paths for the oxidation. In one path, silver ion does not participate prior to or in the rate determining step. The second path has Ag(III) as the reactive silver species. The suggested mechanism for the oxidation is

I. $$H_3PO_3 + H^+ \rightleftharpoons H_4PO_3^+ \quad \text{rapid} \tag{13}$$

$$H_4PO_3^+ \rightleftharpoons (HO)_3P\!: + H^+ \quad \text{r.d.s.} \tag{14}$$

$$(HO)_3P\!: + Ag(II) \longrightarrow \text{products} \tag{15}$$

II. $$2Ag(II) \rightleftharpoons Ag(I) + Ag(III) \qquad (16)$$

$$Ag(III) + H_3PO_3 + H_2O \longrightarrow Ag(I) + H_3PO_4 + 2H^+ \quad \text{r.d.s.} \qquad (17)$$

It is unique for silver not to participate in the rate determining step.

The oxidation of a number of organic substances by Ag(II) have recently been studied.[15,16,17,18]

Honig, Kustin, and Martin[15] studied some hydroxylamine oxidations in $HClO_4$. Reactions of hydroxylamine and o-methylhydroxylamine were 1st order in Ag(II) and 1st order in substrate. The reactions were hydrogen ion inhibited which is explained by the occurrence of two reactive species, Ag^{2+} and $AgOH^+$, the $AgOH^+$ being the more reactive. The rate determining steps are

$$Ag^{2+} + RH_2^+ \longrightarrow Ag(I) + R\cdot + 2H^+ \qquad (18)$$

$$AgOH^+ + RH_2^+ \longrightarrow Ag(I) + R\cdot + H_3O^+ \qquad (19)$$

where RH_2^+ is NH_4OH^+ or $NH_4OCH_3^+$.

The oxidation of various monocarboxylic acids by silver (II) have been studied.

Miller and Morrow[16] studied the formic acid oxidation in nitric acid. The oxidation is 1st order in Ag(II), 1st order in formic acid, and inverse 1st order in H^+. The proposed mechanism is

$$Ag^{2+} + HCO_2^- \longrightarrow Ag^+ + HCO_2^{\cdot} \qquad (20)$$

$$Ag^{2+} + HCO_2^{\cdot} \longrightarrow Ag^+ + H^+ + CO_2 \qquad (21)$$

resulting in the rate law

$$-\frac{d[Ag(II)]}{dt} = \frac{k[Ag(II)][HCOOH]}{\{1+K[NO_3^-]\}[H^+]} . \qquad (22)$$

The reactions of acetic, propionic, n-butyric, isobutyric, and pivalic acids with Ag(II) in perchloric acid were also studied.[17] These oxidations differ from formic acid in that the H^+dependency is complex. The suggested mechanism is similar to that reported by Kustin et al[15] for the hydroxylamine oxidation in which there are two reactive Ag(II) species.

Solid silver (II) picolinate, Bis(α,α'-bipyridine)-silver (II) nitrate, and silver (II) oxide, added to organic solvents, have been used in the heterogeneous oxidative decarboxylation of various organic acids such as pivalic, isobutyric, n-butyric, and acetic acid. The three oxidants, although having different structural types, exhibit common oxidizing properties. The postulated mechanism for the reactions is

$$RCO_2H + Ag(II) \rightleftharpoons H^+ + RCO_2Ag(II) \qquad (23)$$

$$RCO_2Ag(II) \longrightarrow RCO_2\cdot + Ag(I) \qquad (24)$$

$$RCO_2\cdot \longrightarrow R\cdot + CO_2 \qquad (25)$$

$$R\cdot + Ag(II) \longrightarrow R^+ + Ag(I) \qquad (26)$$

The fate of the intermediate cation, R^+, is dependent upon the medium of the reaction. If water were present, the alcohol, ROH, would be a probable end product. The stoichiometric ratio of moles CO_2 : moles of Ag(II) would be

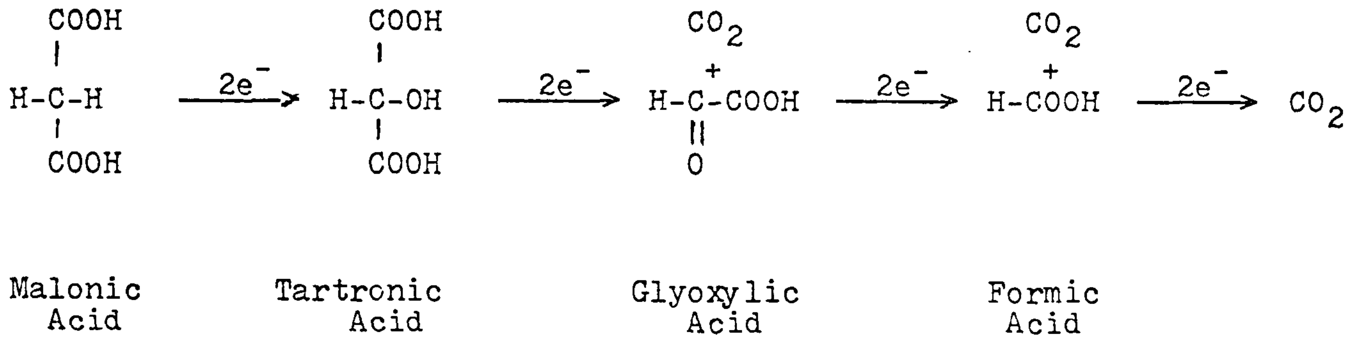
1:2.

A number of stable Ag(II) complexes have been made, usually by the oxidation of silver (I) in the presence of the coordinating ligands.[19-28] The Ag(II)/Ag(I) couple is lowered upon coordination thereby stabilizing the silver (II) species.[29] Silver (II) complexes are generally square planar and have magnetic moments consistent with a d^9 electron configuration.[30]

The oxidation of malonic acid has been studied by many investigators using various oxidizing reagents such as IO_4^- [31], $S_2O_8^{2-}$ [32], MnO_4^- [33], $Cr_2O_7^{2-}$ [34], Mn(III)[35,36], V(V)[37], and Ce(IV)[38,39,40,41]. Malonic acid can undergo an eight electron oxidation to give carbon dioxide as the end product. The suggested pathway for the oxidation is given in Scheme 1. Each step in this scheme consists of a two electron process which occurs in two 1 electron steps when a one electron oxidant is used thereby resulting in free radical intermediates. Most malonic acid oxidations end at the formic acid stage. Only under extreme conditions is there complete oxidation to CO_2.

In some cases, the products were identified by various specific tests as in the examples cited below, while in other cases, the products were not identified but assumed to be the ones given in the general mechanism because of the frequency with which they appear in most of the studied reactions.

SCHEME 1



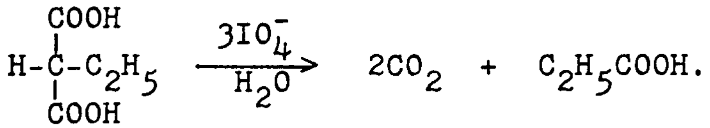
$$\mathrm{CH_2(COOH)_2} \xrightarrow{2e^-} \mathrm{HC(OH)(COOH)_2} \xrightarrow{2e^-} \mathrm{CO_2} + \mathrm{H{-}C({=}O){-}COOH} \xrightarrow{2e^-} \mathrm{CO_2} + \mathrm{H{-}COOH} \xrightarrow{2e^-} \mathrm{CO_2}$$

Malonic acid is oxidized by periodate[31], a two electron oxidant, to give mainly formic acid and CO_2. When the oxidant is in excess, three moles of periodate are consumed and slightly less than two moles of CO_2 are produced per mole of malonic acid. The stoichiometric equation is

$$CH_2(COOH)_2 + 3IO_4^- \longrightarrow HCOOH + 2CO_2 + 3IO_3^- + H_2O. \tag{27}$$

Formic acid was isolated and identified by the Duclaux constants and as the p-toluidide derivative.

The proposed route for the oxidation is that given in Scheme 1. Two pieces of evidence for this scheme were obtained. First, by studying the oxidation rates of the proposed intermediate products, it was found that the oxidation rate of glyoxalic acid is twelve times as rapid as the oxidation rate of tartronic acid which, in turn, is 1.4 times as rapid as the oxidation rate of malonic acid. This is the progression which is expected if the reaction scheme is correct. Second, one mole of ethylmalonic acid is similarly oxidized by three moles of periodate to produce one mole of propionic acid and two moles of CO_2 according to



$$H-\underset{COOH}{\overset{COOH}{C}}-C_2H_5 \xrightarrow[H_2O]{3IO_4^-} 2CO_2 + C_2H_5COOH. \tag{28}$$

The propionic acid was isolated and identified by its Duclaux constants and as the p-toluidide derivative. Propionic acid is the expected product if ethylmalonic acid undergoes oxidation via Scheme 1.

The malonic acid reaction with dichromate[34], $Cr_2O_7^{2-}$, is first order in Cr(VI), first order in malonic acid, and increases in rate with increasing $[H^+]$. The acid catalysis is explained in terms of protonation of malonic acid. This protonated species then reacts with Cr(VI). Spectral evidence was given for a chromium-malonic acid complex.

The oxidation of malonic acid by manganic pyrophosphate[35] and by manganic sulfate[36] have been found to proceed by a common mechanism. The reaction is second order in Mn(II), first order in malonic acid, and inversely dependent upon the [Mn(II)]. The rate is only slightly inhibited by hydrogen ions. The mechanism proposed by Kemp and Waters[36] is

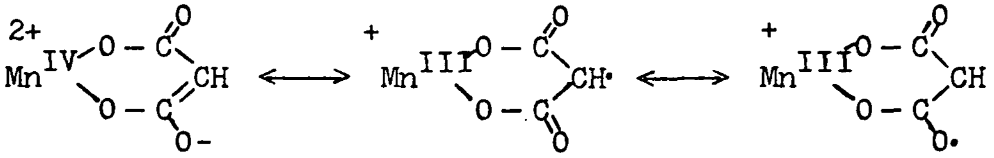
$$Mn^{III}L_3 + CH_2(COOH)_2 \rightleftharpoons L_2Mn^{III}Ma + L \qquad (29)$$

$$Mn^{III}MaL_2 + Mn^{III} \rightleftharpoons Mn^{IV}MaL_2 + Mn^{II} \qquad (30)$$

$$Mn^{IV}MaL_2 \longrightarrow Mn^{II} + \text{products} \qquad (31)$$

$$Mn^{IV}MaL_2 + Mn^{III} \longrightarrow Mn^{II} + Mn^{III} + \text{products} \qquad (32)$$

where $L = SO_4^{2-}$ or $H_2P_2O_7^{2-}$ and Ma represents malonic acid. The rapid complexation of the oxidant, $Mn^{III}L_3$, with malonic acid forming $L_2Mn^{III}Ma$ is followed by oxidation by Mn^{III} to give the complex $Mn^{IV}MaL_2$. This reactive intermediate can act as a free radical in the form of one of its equivalent hybrids;



or can dissociate to give the malonyl free radical by the equation

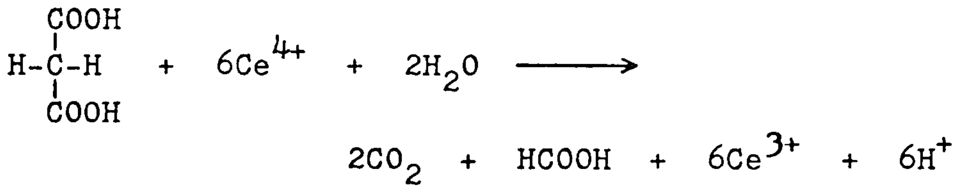
$$\mathrm{Mn^{IV}MaL_2} \rightleftharpoons \mathrm{Mn^{III}L_2} + \cdot\mathrm{CH(COOH)_2}. \qquad (33)$$

The end product, formic acid, was isolated and identified by spot tests.

The oxidation of malonic acid by vanadium (V)[37] in H_2SO_4 differs from the manganese (III) oxidations in that the rate law has both a first order and a second order V(V) term. The rate is unaltered by the lower valence of the oxidant, V(IV), and is greatly accelerated by Mn(II) ions. The basic features of the uncatalyzed reaction are:
a) The formation of a 1:1 $V(OH)_3^{2+}$ - malonic acid complex which dissociates to give the malonyl free radical which in turn reacts further. This reaction sequence gives rise to the first order V(V) term in the rate law. b) The formation of a 2:1 V(V) - malonic acid complex which gives rise to the second order V(V) term of the rate expression. This complex can break down without the formation of a transient free radical thereby explaining the lack of inhibition by V(IV).

Kemp and Waters[37] state that V(IV) does not affect the rate of reaction but they have not supported this with enough data. They give only two V(IV) concentrations (0 and 0.075 M) at two almost identical temperatures (59.8° and 61.6°C). There is a slight trend, in both cases, for rate inhibition with greater [V(IV)]. Additional data should have been acquired to substantiate their conclusion.

The cerium (IV) oxidation of malonic acid in $HClO_4$ has been studied by a few investigators.[38,39,40,41] The stoichiometry of the reaction is:



$$\mathrm{H{-}\underset{COOH}{\overset{COOH}{C}}{-}H} + 6Ce^{4+} + 2H_2O \longrightarrow 2CO_2 + HCOOH + 6Ce^{3+} + 6H^+ \qquad (34)$$

Formic acid was identified as a product by spot tests. The overall reaction proceeds according to Scheme 1. The reaction is first order in Ce(IV), first order in malonic acid, zero order in both Ce(III) and NO_3^-, and is hydrogen ion catalyzed. A mechanism consistent with the experimental results is

$$Ce^{4+} + H_2O \rightleftharpoons CeOH^{3+} + H^+ \qquad (35)$$

$$Ce^{4+} + H_2L \rightleftharpoons CeH_2L^{4+} \qquad (36)$$

$$CeOH^{3+} + H_2L \rightleftharpoons CeHL^{3+} + H_2O \qquad (37)$$

$$CeH_2L^{4+} \rightleftharpoons CeHL^{3+} + H^+ \qquad (38)$$

$$CeH_2L^{4+} \longrightarrow Ce^{III} + H^+ + LH\cdot \quad \text{slow} \qquad (39)$$

$$CeH_2L^{4+} + H^+ \longrightarrow Ce^{III} + 2H^+ + LH\cdot \quad \text{slow} \qquad (40)$$

$$CeHL^{3+} \longrightarrow Ce^{III} + LH\cdot \quad \text{slow} \qquad (41)$$

$$Ce^{IV} + LH\cdot \longrightarrow Ce^{III} + \text{products} \qquad (42)$$

where H_2L is malonic acid and $LH\cdot$ is a free radical. Since this is the mechanism for the first step of Scheme 1, the end product is tartronic acid.

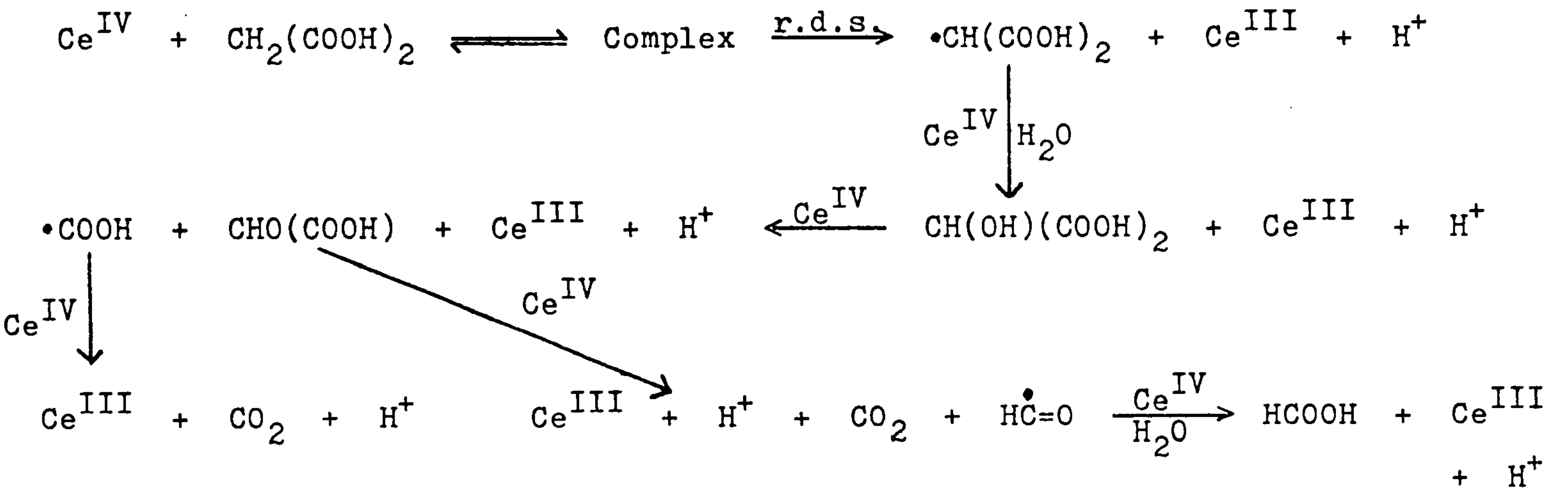
In perchloric acid, Ce(IV) exists as both the hydrated ion and the first hydrolysis product formed by equation 35, both of which can complex with malonic acid (equations 36 and 37, respectively) to give CeH_2L^{4+} and $CeHL^{3+}$, respectively. Both complexes will dissociate in the rate determining steps to give Ce(III) and a free radical, R• (equations 39 and 41). The CeH_2L^{4+} dissociation can be acid catalyzed (equation 40). The free radical formed will react with another Ce(IV) and a water molecule forming tartronic acid. The precursor of tartronic acid is the malonyl free radical, formed in equations 39, 40, and 41. McAuley and coworkers[41] proved this to be the case by obtaining the ESR spectrum of the free radical. It was observed to be a doublet consistent with the radical $\cdot CH(COOH)_2$. The total oxidation reaction is presented in Scheme 2.

In summary, when the oxidant is capable of forming complexes, malonic acid will form a complex prior to the electron transfer step. Such was the case with Mn(III), V(V), and Ce(IV). In addition, when one electron oxidants are used, the malonyl free radical is believed to be formed in the rate determining step.

Very limited research has been done on substituted malonic acid derivatives.

It is the intent of this thesis to compare the kinetics of the silver (II) oxidation of malonic acid, its methyl-, ethyl-, dimethyl-, and diethyl-derivatives. Of major interest will be the effect that substitution has on the qualitative and quantitative aspects of the mechanism.

Scheme 2


Ce^IV + CH2(COOH)2 ⇌ Complex
r.d.s.
•CH(COOH)2 + Ce^III + H+
Ce^IV H2O
CH(OH)(COOH)2 + Ce^III + H+
Ce^IV
•COOH + CHO(COOH) + Ce^III + H+
Ce^IV
Ce^IV
Ce^III + CO2 + H+
Ce^III + H+ + CO2 + HĊ=O
Ce^IV H2O
HCOOH + Ce^III + H+

EXPERIMENTAL SECTION

Materials: All chemicals used were either reagent grade or of certified purity.

Silver (II) solutions were prepared just prior to use by adding the appropriate solution to previously weighed amounts of silver (II) oxide (Alfa Inorganics). All organic acid solutions (Aldrich Chemical Co.) were also prepared just prior to use.

The malonic acid was purified by precipitating out its calcium salt to get rid of chloride ion impurities. All the organic acids were recrystallized from water.

All acid solutions were prepared using stock solutions of nitric acid (Fisher Chemical Co.) and/or perchloric acid (J. T. Baker Chemical Co.).

Silver (I) nitrate (Amend Drug and Chemical Co.) was added to all solutions in order to stabilize the Ag(II). Sodium nitrate (Mallinckrodt Chemical Co.) were used to keep the ionic strength fixed.

The method used to determine the silver (II) concentration in acid media involves adding aliquot portions of silver (II) solution to a given volume of 0.15 M cerium (III) nitrate solution (Fisher Chemical Co.). Silver (II) oxidizes cerium (III) quantitatively to cerium (IV) via the following reaction

$$\mathrm{Ag(II)} + \mathrm{Ce(III)} \longrightarrow \mathrm{Ag(I)} + \mathrm{Ce(IV)}. \quad (43)$$

The resultant absorbance, due to the cerium (IV) produced from this reaction, is promptly measured on a Beckman DU Spectrophotometer. The absorbance is related to the [Ce(IV)] through a Beer's Law Curve, and the silver (II) concentration is back-calculated.

Kinetic Measurements: The Aminco-Morrow Stopped Flow Apparatus[42] was used for all kinetic measurements. It is shown schematically in Figure 3. The use of this instrument permits the rapid mixing of equal volumes of the two reactants.

The two reactant solutions, contained in the drive syringes, are pneumatically forced into a teflon mixing chamber. They then enter a quartz windowed observation cell with a path length of 10 mm. The dead time, the time it takes the solution to reach the point of observation from the point of mixing, is two milliseconds. The efficiency of mixing is greater than 98% in less than one millisecond after initial contact.

The mixed reactants enter an exhaust chamber after leaving the observation cell. This advances the piston of the stopping syringe which contacts a micrometer, closing a switch, and thereby triggering a storage oscilloscope. About 0.1 ml. of each solution is used for each run. This amount is sufficient to flush previously spent solutions and leave a fresh reaction mixture in the observation cell. The solutions only come in contact with inert materials such as Kel-F, teflon, and quartz. Thermostating of solutions is

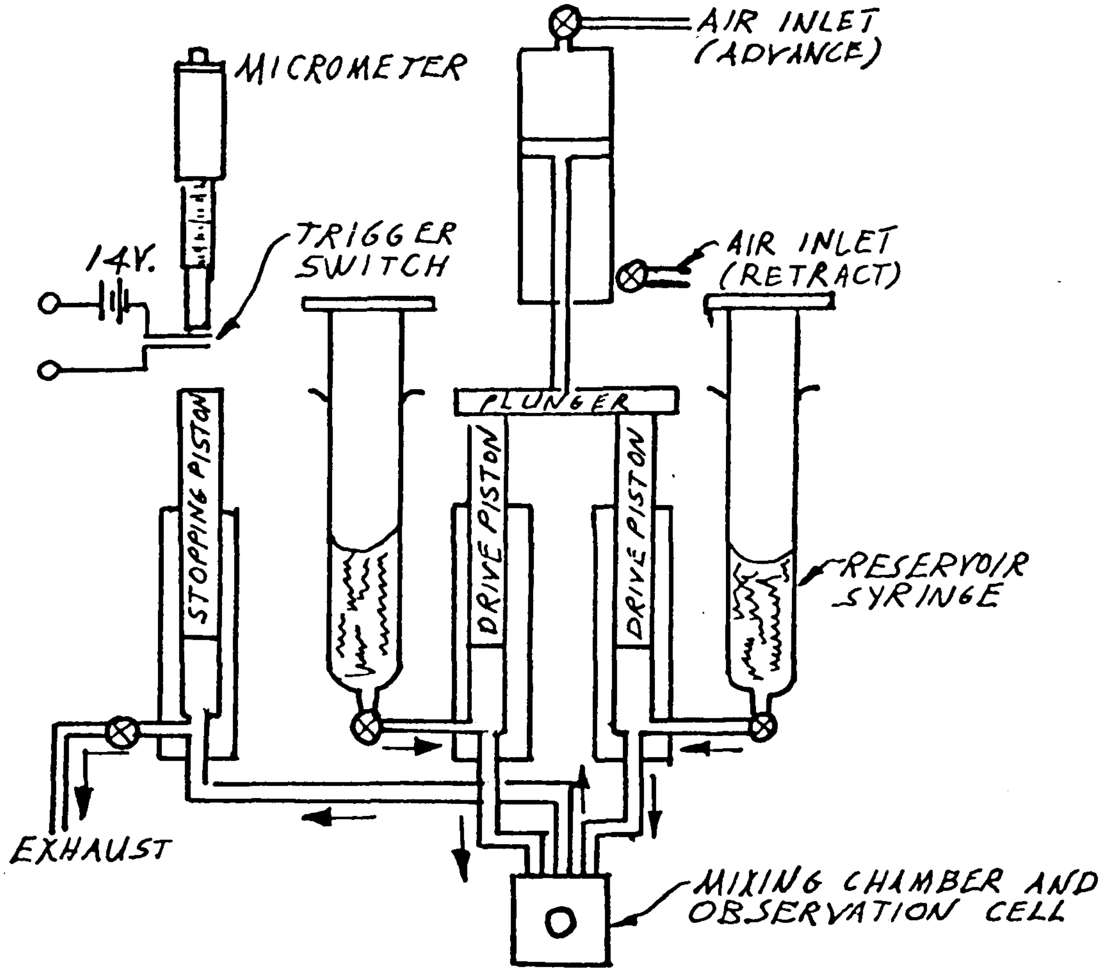
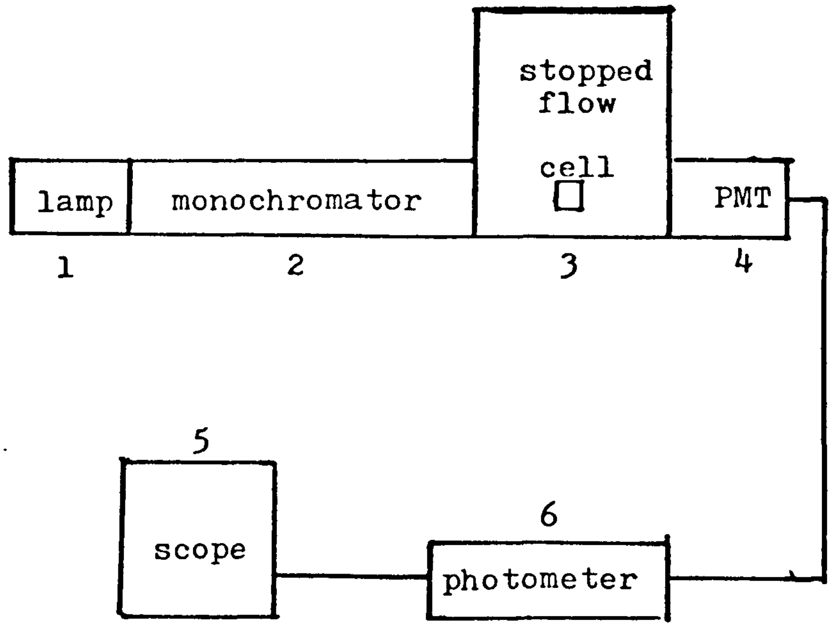


Figure 3. Schematic Diagram of an Aminco-Morrow Stopped-Flow Apparatus.

achieved by the circulation of water through holes drilled into the aluminum block in which the drive syringes are mounted.

The entire experimental system is illustrated in Figure 4. Light from a tungsten lamp, powered by a Hewlett-Packard 6274B DC Power Supply, passes through an Aminco Minimonochromator to produce monochromatic light of the desired wavelength which then passes through the observation cell. A Hamamatsu R-136 Photomultiplier Tube (PMT) powered by an Aminco Photomultiplier High Voltage Power Supply was used to determine the amount of transmitted light. The PMT output signal is fed into an Aminco Linear-Log High Performance Kinetic Photometer. The signal is filtered and converted to a logarithmic (absorbance) signal which is displayed on a Tektronix E103 N Singlebeam Storage Oscilloscope. A Polaroid Camera was used to photograph the kinetic trace for future analysis.

Stoichiometric measurements: A gas buret, shown in Figure 5, was used to determine the stoichiometry of the reactions studied. Known amounts of the two reactants are mixed and the volume of carbon dioxide evolved at a known pressure and temperature is measured. From the volume of carbon dioxide liberated, the number of moles is calculated and the mole ratio of CO_2:Ag(II) is determined.



1 - The light source is a tungsten lamp powered by a Hewlett-Packard 6274B DC power supply.
2 - The monochromator is an Aminco Minimonochromator.
3 - The mixing system is an Aminco-Morrow Stopped-Flow Apparatus. The dead time is 2msec. and the mixing time is less than 1 msec. with better than 98% efficiency.
4 - The detector is a Hamamatsu R-136 Photomultiplier Tube powered by an Aminco Photomultiplier High Voltage Power Supply.
5 - An Aminco Linear-Log Photometer permits offsetting, change of bandwidth, and selection of output as % transmittance or as absorbance.
6 - The change in absorbance is displayed as a trace on a Tektronix Storage Oscilloscope.

Figure 4. Schematic Diagram of the Experimental System

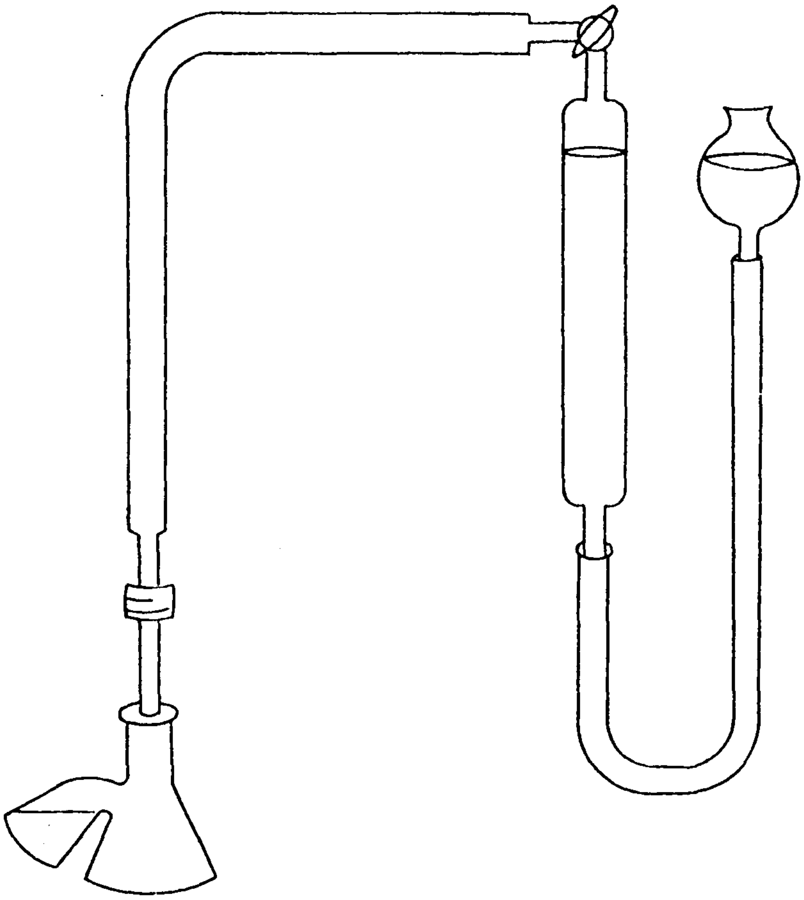


Figure 5. Gas Buret Apparatus

RESULTS SECTION

Stoichiometry: The stoichiometry was determined under conditions similar to those established for the kinetic experiments. For malonic, methylmalonic and ethylmalonic acids the results are consistent with the overall reaction

$$RCH(COOH)_2 + 6Ag(II) + 2H_2O \longrightarrow RCOOH + 2CO_2 + 6Ag(I) + 6H^+ \quad (44)$$

where R = H, CH_3, or C_2H_5. The mole ratio of CO_2 produced to silver (II) consumed is 1:3. For dimethylmalonic and diethylmalonic acids, the results are consistent with the reaction

$$R_2C(COOH)_2 + 2Ag(II) + H_2O \longrightarrow R_2C(COOH)OH + CO_2 + 2Ag(I) + 2H^+ \quad (45)$$

where the mole ratio of CO_2 produced to silver (II) consumed is 1:2. These results are given in Tables 1-5.

Kinetics: The loss of silver (II) was monitored at 370 nm. The reaction was studied under pseudo-first-order conditions with silver (II) in limiting quantity. The kinetic data was analyzed by means of the half-life method.

Under the experimental kinetic conditions, the reaction is first order in silver (II) in the concentration range of 1.0×10^{-4} to 2.0×10^{-3} M, first order in LH_2 regardless of $[LH_2]$ where LH_2 is malonic acid (MH_2), methylmalonic acid (MMH_2), ethylmalonic acid (EMH_2), dimethylmalonic acid ($DMMH_2$), or diethylmalonic acid ($DEMH_2$), and zero order in silver (I) in the concentration range of 0.005 to 0.2 M. Below 0.005 M Ag(I), deviations from first order Ag(II) dependencies are observed. The kinetic data are given in Tables 6-10.

The observed pseudo-first-order rate constant, $k_{obs.}$, is defined by equation 46.

$$\frac{-d[Ag(II)]}{dt} = k_{obs.}[Ag(II)] \qquad (46)$$

The second order rate constant, $k_{H,N}$, which includes both the hydrogen ion and nitrate ion dependencies is given by equation 47.

$$k_{obs.} = k_{H,N}[LH_2] \qquad (47)$$

The plots of $k_{obs.}$ vs. $[LH_2]$ (shown in Figures 6-10) for the five organic substrates are linear thereby confirming the first order dependency in LH_2. The calculated values of $k_{H,N}$ for MH_2, MMH_2, EMH_2, $DMMH_2$, and $DEMH_2$ are 8.8, 7.0, 10.8, 121, and 228 $M^{-1}sec^{-1}$, respectively.

Isotope Study: The value of $k_{H,N}$ for malonic acid is 2.8 times greater than $k_{H,N}$ if deuterated malonic acid is used. This indicates that for the malonic acid oxidation, the slow step involves the loss of a methylene hydrogen.

Acidity Dependency: At constant nitrate ion concentration, $k_{H,N}$ behaves differently for malonic acid as compared to its mono- and disubstituted derivatives. For MH_2, $k_{H,N}$ increases linearly with $[H^+]$ according to equation 48

$$k_{H,N} = A[H^+] + B \qquad (48)$$

where A and B are constants at constant nitrate ion concentration. For the substituted derivatives, however, the reaction was inhibited by hydrogen ions. This will be discussed later on. Tables 11-15 contain the hydrogen ion data.

Nitrate Ion Dependency: Tables 16-20 show the effect of nitrate ion upon the value of $k_{H,N}$ at constant acidity. The data obeys equation 49

$$k_{H,N} = \frac{1}{a + b[NO_3^-]} \tag{49}$$

where a and b are constants independent of nitrate ion concentration. The linear form of equation 49 is

$$\frac{1}{k_{H,N}} = a + b[NO_3^-]. \tag{50}$$

TABLE 1

CO_2:Ag(II) MOLE RATIO FOR THE MALONIC ACID OXIDATION[a]

moles Ag(II) x 10^3	moles MH_2 x 10^3	moles CO_2 x 10^4	mole ratio CO_2:Ag(II)
0.94	17.8	3.30	1:2.8
1.86	4.46	6.53	1:2.9
1.92	8.92	7.03	1:2.7

a - All experiments were performed with $[HNO_3]$ = 4.0 M, $[AgNO_3]$ = 0.100 M, and I = 4.1 M, where I is ionic strength.

TABLE 2

CO_2:Ag(II) MOLE RATIO FOR THE METHYLMALONIC ACID OXIDATION[a]

moles Ag(II) x 10^3	moles MMH_2 x 10^3	moles CO_2 x 10^4	mole ratio CO_2:Ag(II)
1.86	2.25	6.11	1:3.0
1.86	4.50	6.16	1:3.0
1.88	6.74	6.24	1:3.0
1.88	8.99	6.80	1:2.8
1.88	18.0	6.32	1:3.0

a- All experiments were performed with $[HNO_3]$ = 4.0 M and $[AgNO_3]$ = 0.100 M, and I = 4.1 M.

TABLE 3

CO_2:Ag(II) MOLE RATIO FOR THE ETHYLMALONIC ACID OXIDATION[a]

moles Ag(II) x 10^3	moles EMH_2 x 10^3	moles CO_2 x 10^4	mole ratio CO_2:Ag(II)
1.70	2.18	5.81	1:2.9
1.75	4.36	5.77	1:3.0
1.76	6.54	6.05	1:2.9
1.78	8.72	6.24	1:2.9

a - All experiments were performed with $[HNO_3]$ = 4.0 M, $[AgNO_3]$ = 0.100 M, and I = 4.1 M.

TABLE 4

CO_2:Ag(II) MOLE RATIO FOR THE DIMETHYLMALONIC OXIDATION[a]

moles Ag(II) x 10^3	moles $DMMH_2$ x 10^3	moles CO_2 x 10^4	mole ratio CO_2:Ag(II)
1.85	2.25	8.55	1:2.2
1.72	5.50	8.87	1:1.9
1.87	5.50	9.19	1:2.0
1.85	6.74	8.75	1:2.1
1.86	6.74	8.99	1:2.1
1.88	8.99	9.23	1:2.0

a - All experiments were performed with $[HNO_3]$ = 4.0 M and $[AgNO_3]$ = 0.100 M, and I = 4.1 M.

TABLE 5

CO_2:Ag(II) MOLE RATIO FOR THE DIETHYLMALONIC OXIDATION[a]

moles Ag(II) x 10^3	moles $DEMH_2$ x 10^3	moles CO_2 x 10^4	mole ratio CO_2:Ag(II)
1.63	2.20	7.46	1:2.2
1.66	4.40	7.50	1:2.2
1.62	6.61	7.78	1:2.1
1.77	8.81	8.38	1:2.1
1.01	8.81	4.99	1:2.0

a - All experiments were performed with $[HNO_3] = 4.0$ M and $[AgNO_3] = 0.100$ M, and I = 4.1 M.

TABLE 6

KINETIC DATA
FOR THE MALONIC ACID OXIDATION[a]

[MH_2] x 10_3, M	[Ag(II)] x 10^3, M	[Ag(I)], M	$k_{obs.}$, sec^{-1}	$k_{H,N}$, $M^{-1}sec^{-1}$
50.0	0.11	0.0100	0.36	7.2
50.0	0.28	0.0100	0.38	7.6
50.0	0.51	0.0100	0.34	6.8
50.0	0.81	0.0100	0.34	6.8
50.0	0.93	0.0100	0.33	6.6
5.00	0.60	0.100	0.046	9.2
10.0	0.60	0.100	0.087	8.7
25.0	0.60	0.100	0.22	8.8
50.0	0.60	0.100	0.50	10
75.0	0.60	0.100	0.73	9.7
100	0.60	0.100	0.82	8.2
125	0.60	0.100	1.2	9.6
150	0.60	0.100	1.4	9.3
200	0.60	0.100	1.7	8.5
25.0	1.0	0.0100	0.20	8.0
25.0	1.0	0.0200	0.22	8.8
25.0	1.0	0.0750	0.24	9.6
25.0	1.0	0.100	0.30	12
25.0	1.0	0.150	0.26	10
25.0	1.0	0.200	0.23	9.2
2.50	1.0	0.100	0.015	6.1[b]
5.00	1.0	0.100	0.023	4.6[b]
12.5	1.0	0.100	0.064	5.1[b]
25.0	1.0	0.100	0.087	3.6[b]
50.0	1.0	0.100	0.15	3.0[b]
100	1.0	0.100	0.33	3.3[b]

a - [HNO_3] = 4.0 M and I = 6.6 M.

b - Deuterated malonic acid was used in these experiments.

TABLE 7

KINETIC DATA
FOR THE METHYLMALONIC ACID OXIDATION

$[MMH_2]$ x 10^3, M	$[Ag(II)]$ x 10^3, M	$[Ag(I)]$, M	$k_{obs.}$, sec^{-1}	$k_{H,N}$, $M^{-1}sec^{-1}$
2.50	2.0	0.100	0.0197	7.88
12.5	2.0	0.100	0.0924	7.39
25.0	2.0	0.100	0.187	7.48
50.0	2.0	0.100	0.346	6.93
100	2.0	0.100	0.711	7.11
25.0	1.0	0.0500	0.198	7.92
25.0	1.0	0.0100	0.204	8.16
25.0	1.0	0.00500	0.213	8.53
25.0	1.5	0.0100	0.187	7.48

a - $[HNO_3]$ = 4.0 M and I = 6.6 M.

TABLE 8

KINETIC DATA
FOR THE ETYLMALONIC ACID OXIDATION[a]

$[EMH_2]$ x 10^3, M	$[Ag(II)]$ x 10^3, M	$[Ag(I)]$, M	$k_{obs.}$, sec^{-1}	$k_{H,N}$, $M^{-1}sec^{-1}$
2.50	1.0	0.100	0.0289	11.6
5.00	1.0	0.100	0.0619	12.4
7.50	1.0	0.100	0.0815	10.9
10.0	1.0	0.100	0.111	11.1
12.5	1.0	0.100	0.144	11.5
20.0	1.0	0.100	0.204	10.2
25.0	1.0	0.100	0.283	11.3
25.0	0.50	0.00500	0.26	10
25.0	0.50	0.0100	0.25	10
25.0	0.50	0.0500	0.24	10
25.0	0.25	0.0500	0.23	9.2
25.0	0.75	0.0100	0.23	9.2

a - $[HNO_3]$ = 4.0 M and I = 6.6 M.

TABLE 9

KINETIC DATA
FOR THE DIMETHYLMALONIC ACID OXIDATION[a]

$[DMMH_2]$ x 10^3, M	$[Ag(II)]$ x 10^3, M	$[Ag(I)]$, M	$k_{obs.}$, sec^{-1}	$k_{H,N}$ x 10^{-2}, $M^{-1}sec^{-1}$
1.50	0.50	0.100	0.167	1.1
2.50	0.50	0.100	0.292	1.2
5.00	0.50	0.100	0.498	1.0
10.0	0.50	0.100	0.930	.93
12.5	0.50	0.100	1.49	1.2
20.0	0.65	0.100	2.66	1.3
20.0	0.80	0.100	2.89	1.4
20.0	1.0	0.100	2.52	1.3
20.0	2.0	0.100	2.31	1.2
20.0	1.0	0.00500	2.52	1.3
20.0	1.0	0.0100	2.39	1.2
20.0	1.0	0.0500	2.57	1.3
20.0	1.0	0.100	2.31	1.2

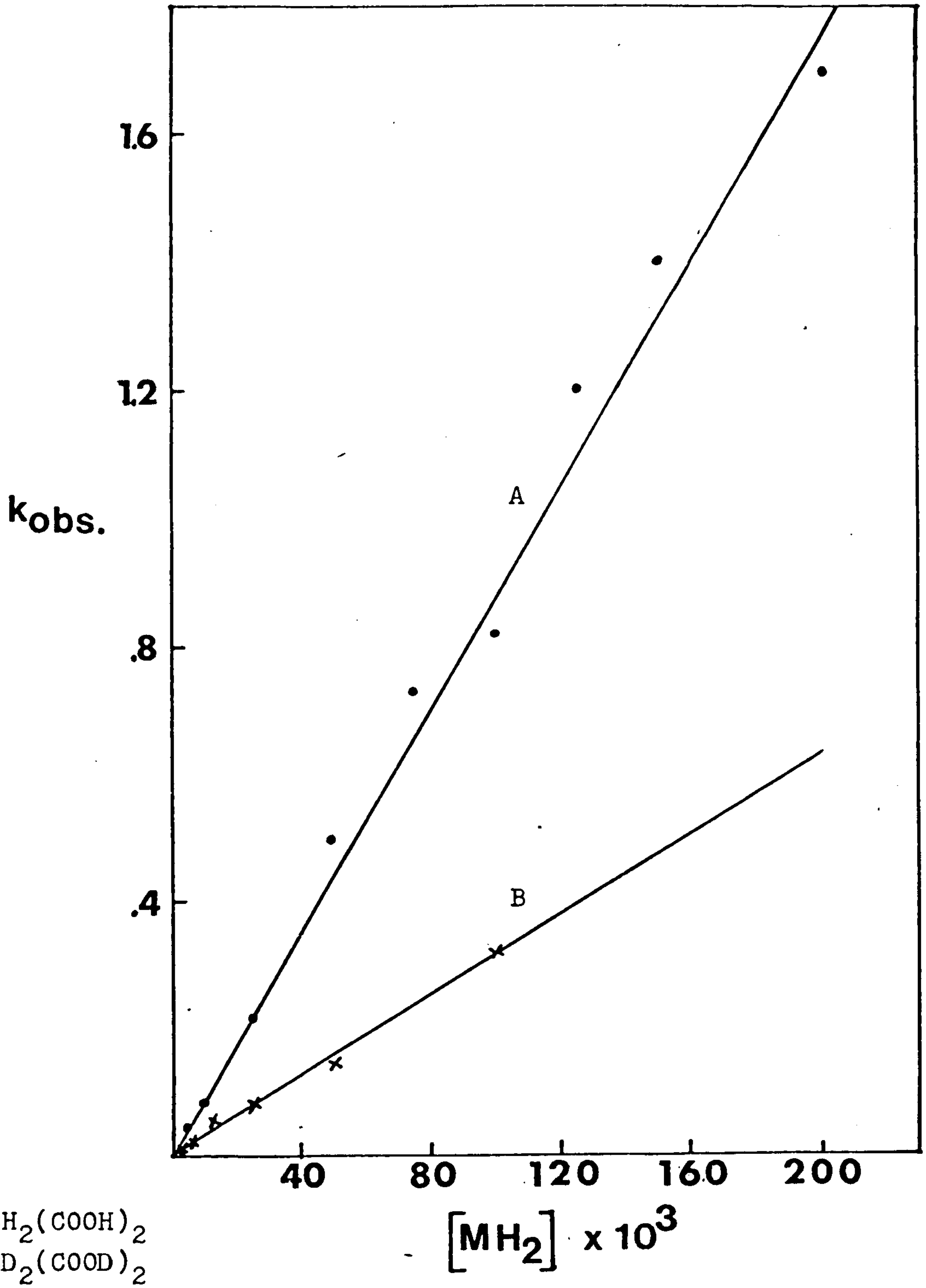
a - $[HNO_3]$ = 4.0 M and I = 6.6 M.

TABLE 10

KINETIC DATA FOR THE DIETHYLMALONIC ACID OXIDATION[a]

$[DEMH_2]$ x 10^3, M	$[Ag(II)]$ x 10^3, M	$[Ag(I)]$, M	$k_{obs.}$, sec^{-1}	$k_{H,N}$ x 10^{-2}, $M^{-1}sec^{-1}$
2.50	0.50	0.100	0.630	2.5
7.50	0.50	0.100	1.69	2.2
12.5	0.50	0.100	2.57	2.1
25.0	0.50	0.100	5.59	2.2
20.0	0.65	0.100	4.78	2.4
20.0	0.80	0.100	4.62	2.3
20.0	1.0	0.100	4.56	2.3
20.0	2.0	0.100	4.62	2.3
20.0	1.0	0.00500	5.92	2.9
20.0	1.0	0.0100	4.78	2.4
20.0	1.0	0.0500	4.78	2.4

a - $[HNO_3] = 4.0$ M and $I = 6.6$ M.



A - $CH_2(COOH)_2$
B - $CD_2(COOD)_2$

Figure 6. $k_{obs.}$ vs. $[MH_2]$

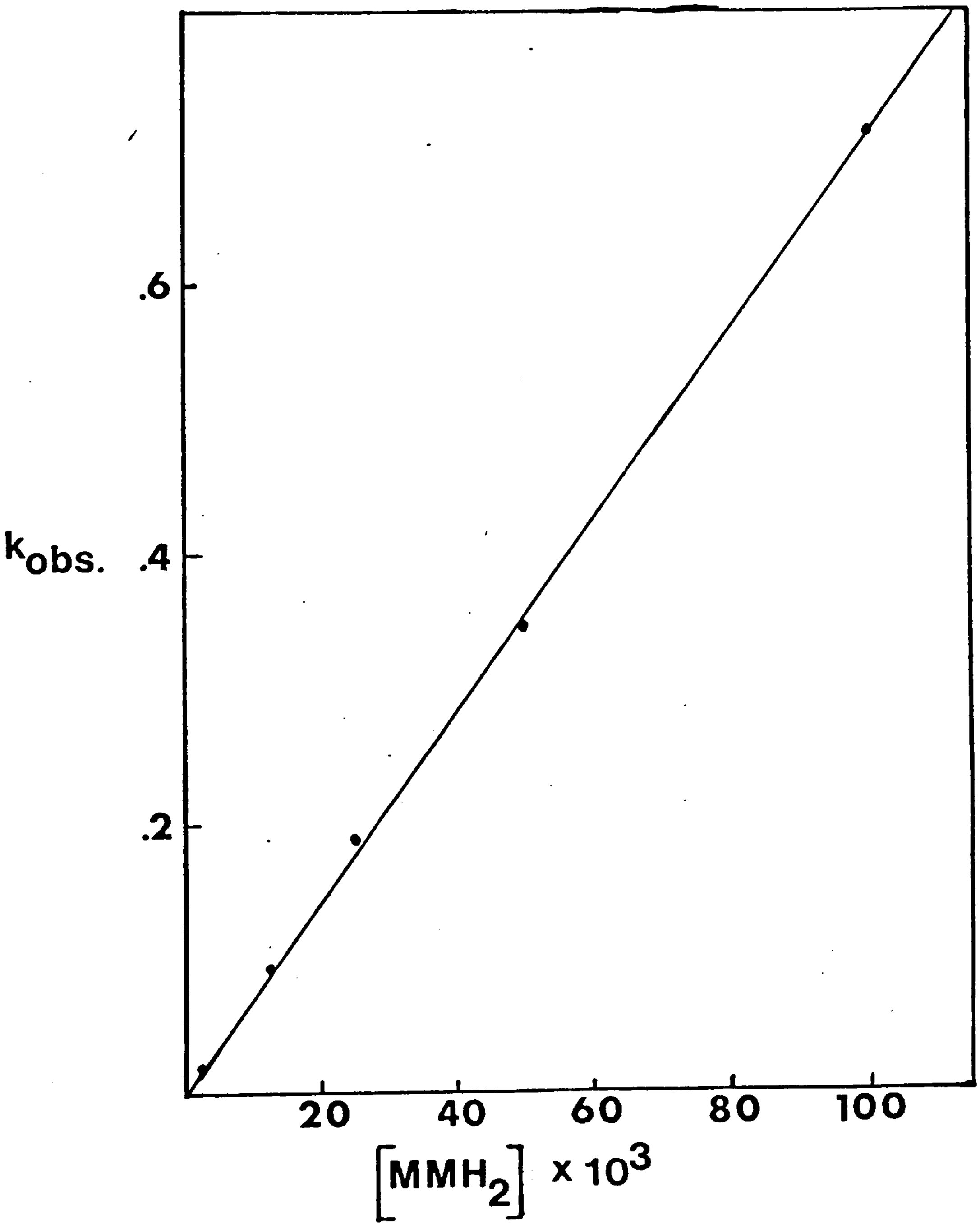


Figure 7. $k_{obs.}$ vs. $[MMH_2]$

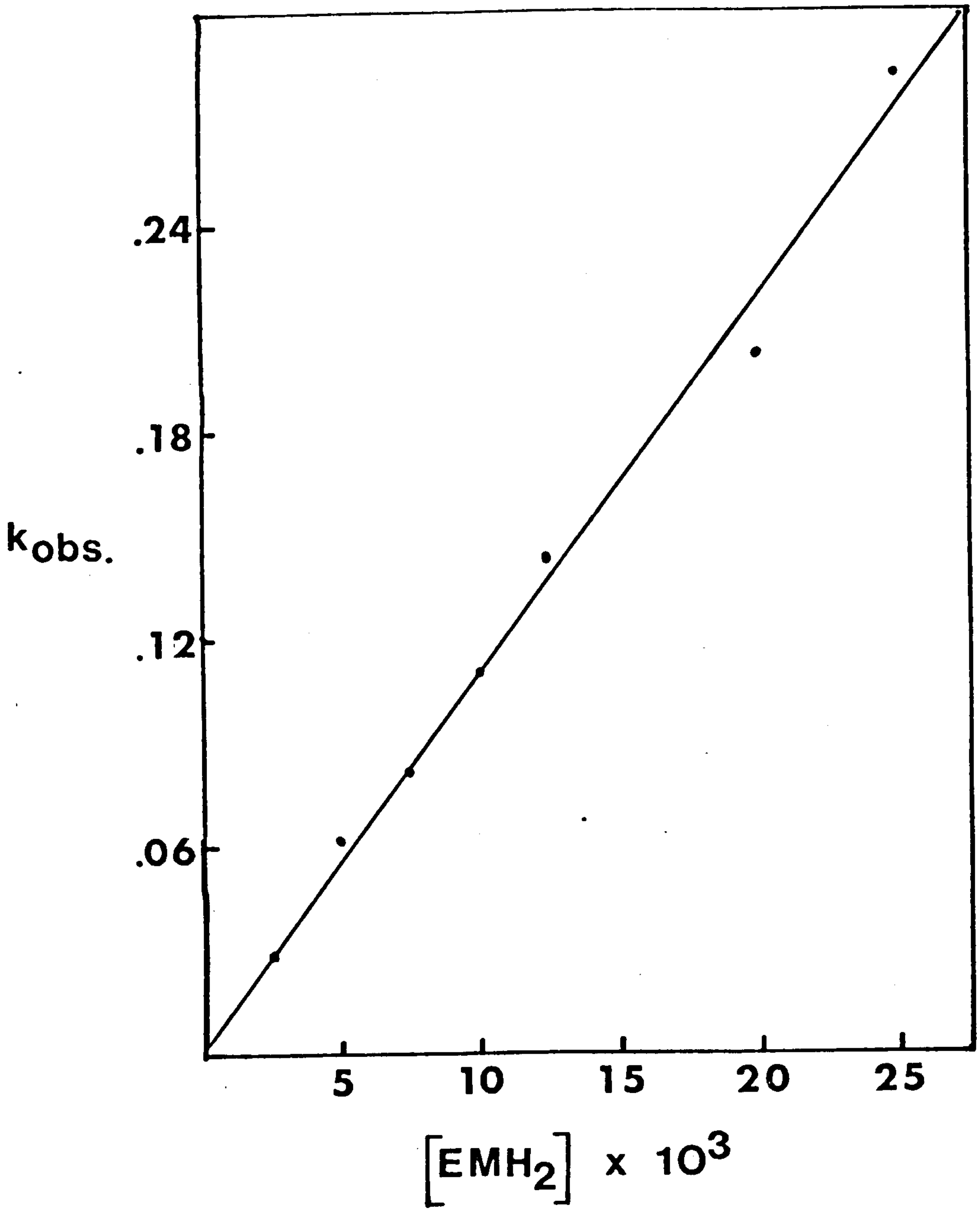


Figure 8. $k_{obs.}$ vs. $[EMH_2]$

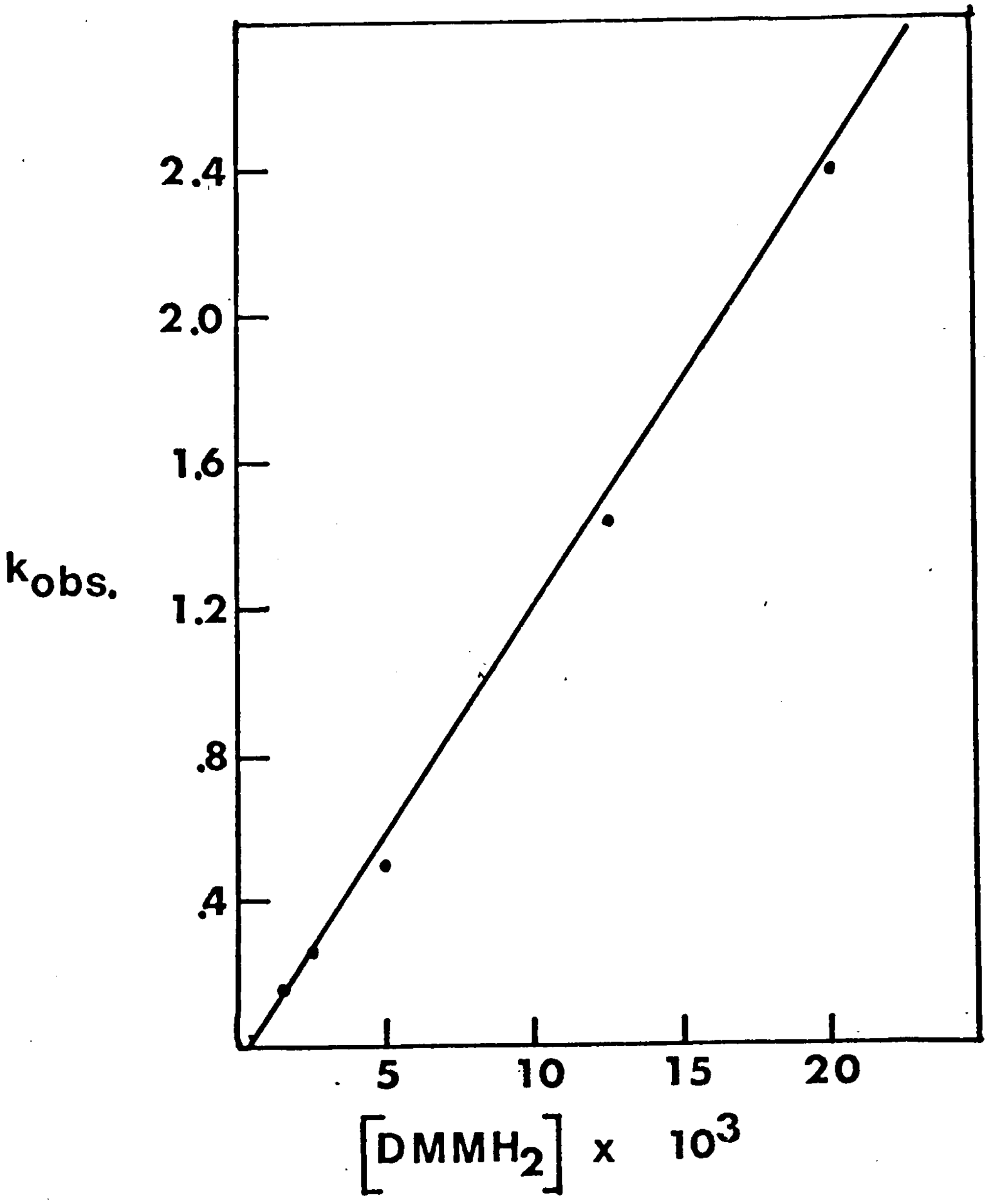


Figure 9. $k_{obs.}$ vs. $[DMMH_2]$

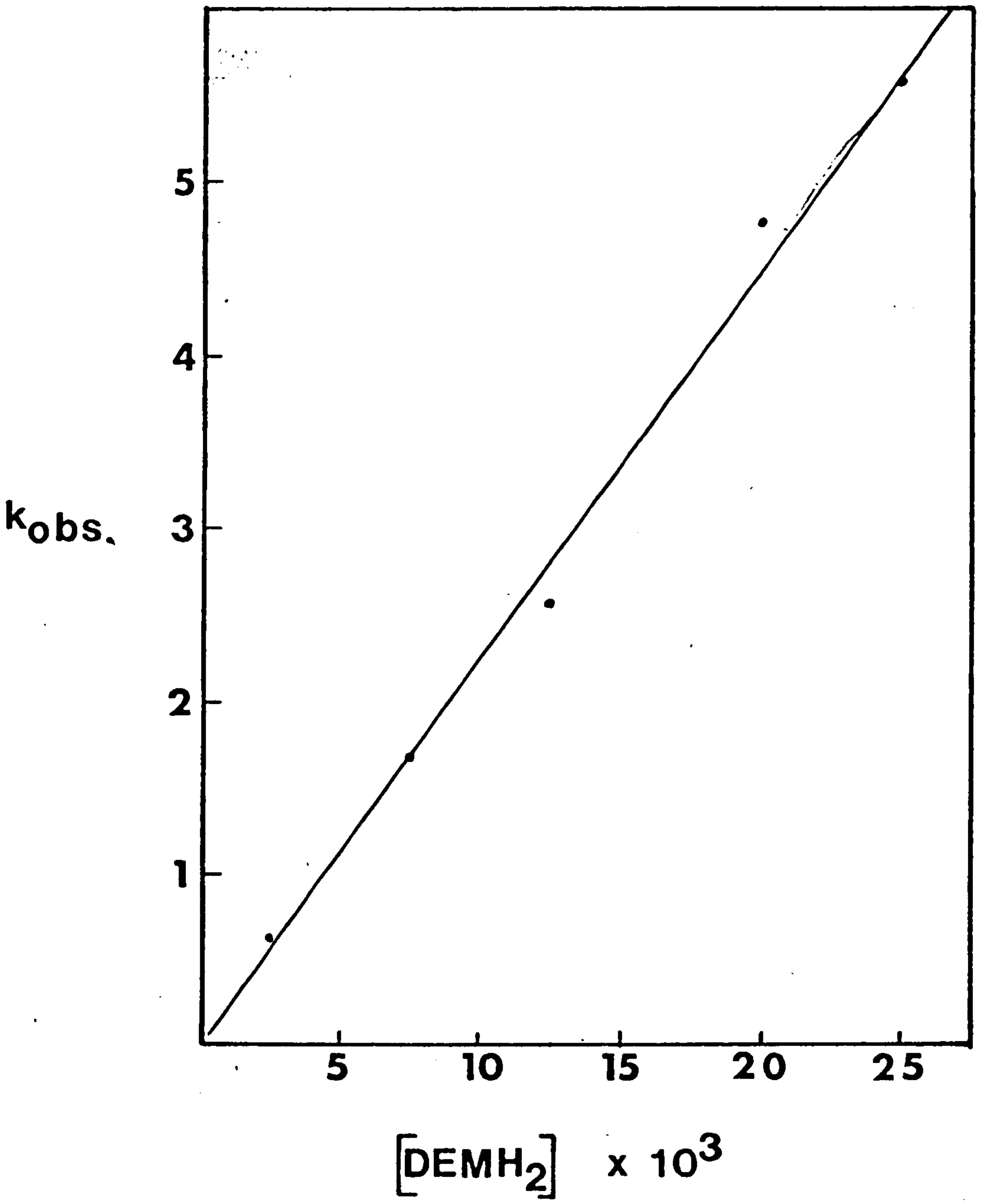


Figure 10. $k_{obs.}$ vs. $[DEMH_2]$

TABLE 11

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

$[H^+]$, M	$k_{obs.}$, sec^{-1}	$k_{H,N}$, $M^{-1}sec^{-1}$
6.0	0.161	8.05
5.0	0.154	7.70
4.5	0.150	7.50
4.0	0.146	7.30
3.0	0.139	6.95
2.5	0.133	6.65
2.0	0.131	6.55

a - $[MH_2]$ = 0.0200 M, $[Ag(II)]$ = 0.0005 M, $[Ag(I)]$ = 0.0100M, $[NO_3^-]$ = 6.6 M, and I = 6.6 M.

TABLE 12

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

$[H^+]$, M	$k_{obs.}$, sec^{-1}	$k_{H,N}$, $M^{-1}sec^{-1}$	$k_{H,N}([H^+]+K_{57}[H^+][NO_3^-]+K_{56})$[b]
6.5	0.139	6.95	330
6.0	0.139	6.95	305
5.0	0.151	7.55	277
4.5	0.153	7.65	253
4.0	0.165	8.25	243
3.0	0.173	8.66	193
2.5	0.192	9.60	180
2.0	0.224	11.2	169

a - $[MMH_2] = 0.0200$ M, $[Ag(II)] = 0.0005$ M, $[Ag(I)] = 0.0100$ M, $[NO_3^-] = 6.6$ M, and $I = 6.6$ M.

b - K_{56} and K_{57} are the equilibrium constants of equations 56 and 57, respectively

TABLE 13

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

$[H^+]$, M	$k_{obs.}$, sec^{-1}	$k_{H,N}$, $M^{-1}sec^{-1}$	$k_{H,N}([H^+]+K_{57}[H^+][NO_3^-]+K_{56})$[b]
6.0	0.187	9.35	410
5.0	0.204	10.2	374
4.5	0.213	10.7	354
4.0	0.231	11.6	342
3.0	0.263	13.2	294
2.5	0.301	15.0	280
2.0	0.355	17.8	269

a - $[EMH_2] = 0.0200$ M, $[Ag(II)] = 0.0005$ M, $[Ag(I)] = 0.0100$ M, $[NO_3^-] = 6.6$ M, and I = 6.6 M.

b - K_{56} and K_{57} are the equilibrium constants of equations 56 and 57, respectively.

TABLE 14

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

$[H^+]$, M	$k_{obs.}$, sec^{-1}	$k_{H,N}$, $M^{-1}sec^{-1}$	$1/k_{H,N}$ x 10^3, M sec
6.5	1.32	66.0	15.2
6.0	1.39	69.5	14.4
5.0	1.78	89.0	11.2
4.5	1.82	91.0	11.0
4.0	1.98	99.0	10.1
3.0	2.48	124	8.06
2.5	3.30	165	6.06
2.0	3.85	192	5.20

a - $[DMMH_2]$ = 0.0200 M, $[Ag(II)]$ = 0.0005 M, $[Ag(I)]$ = 0.0100 M, $[NO_3^-]$ = 6.6 M, and I = 6.6 M

TABLE 15

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

$[H^+]$, M	$k_{obs.}$, sec^{-1}	$k_{H,N}$, $M^{-1}sec^{-1}$	$1/k_{H,N}$ x 10^3, M sec
6.5	2.57	128	7.78
6.0	2.77	138	7.22
5.0	3.30	165	6.06
4.5	3.46	173	5.78
4.0	4.08	204	4.90
3.0	5.33	266	3.76
2.5	6.03	302	3.32
2.0	8.40	420	2.38

a- $[DEMH_2]$ = 0.0200 M, $[Ag(II)]$ = 0.0005 M
$[Ag(I)]$ = 0.0100 M, $[NO_3^-]$ = 6.6 M, and I = 6.6 M.

TABLE 16

DEPENDENCE OF $k_{H,N}$ ON THE NITRATE ION CONCENTRATION FOR THE MALONIC ACID OXIDATION[a]

	$[NO_3^-]$, M	$k_{obs.}$, sec^{-1}	$k_{H,N}$, $M^{-1}sec^{-1}$	$1/k_{H,N}$, M sec
$[H^+]$ = 2.0 M				
	2.60	0.216	10.8	0.0924
	3.60	0.139	6.95	0.144
	4.60	0.126	6.30	0.159
	5.60	0.0990	4.95	0.202
	6.60	0.0894	4.47	0.224
$[H^+]$ = 4.0 M				
	2.60	0.216	10.8	0.0924
	3.60	0.182	9.10	0.109
	4.60	0.161	8.05	0.124
	5.60	0.154	7.70	0.129
	6.60	0.144	7.20	0.138
$[H^+]$ = 6.0 M				
	2.60	0.185	9.25	0.108
	3.60	0.173	8.65	0.115
	4.60	0.163	8.15	0.123
	5.60	0.154	7.70	0.129
	6.60	0.146	7.30	0.137

a - $[MH_2]$ = 0.0200 M, [Ag(II)] = 0.00100 M, [Ag(I)] = 0.0100 M, and I = 6.6 M.

TABLE 17

DEPENDENCE OF $k_{H,N}$ ON THE NITRATE ION CONCENTRATION FOR THE METHYLMALONIC ACID OXIDATION[a]

	$[NO_3^-]$, M	$k_{obs.}$, sec^{-1}	$k_{H,N}$, $M^{-1}sec^{-1}$	$1/k_{H,N}$, M sec
$[H^+]$ = 2.0 M				
	1.60	0.770	38.5	0.0260
	2.60	0.578	28.9	0.0346
	3.60	0.408	20.4	0.0490
	4.60	0.301	15.0	0.0662
	5.60	0.248	12.4	0.0808
	6.60	0.224	11.2	0.0894
$[H^+]$ = 4.0 M				
	1.60	0.554	27.7	0.0360
	2.60	0.364	18.2	0.0542
	3.60	0.277	13.8	0.0722
	4.60	0.217	10.8	0.0922
	5.60	0.187	9.35	0.107
	6.60	0.159	7.95	0.125
$[H^+]$ = 6.0 M[b]				
	0.600	0.320	128	0.00781
	1.60	0.120	48.0	0.0208
	2.60	0.0710	28.4	0.0352
	3.60	0.0537	21.5	0.0465
	4.60	0.0498	19.9	0.0502
	5.60	0.0357	14.3	0.0700
	6.60	0.0270	10.8	0.0926

a - $[MMH_2]$ = 0.0200 M, [Ag(II)] = 0.0015 M, [Ag(II)] = 0.0100M, and I = 6.6 M

b - $[MMH_2]$ = 0.0025 M, [Ag(II)] = 0.00050M, [Ag(I)] = 0.100 M, and I = 6.6 M

TABLE 18

DEPENDENCE OF $k_{H,N}$ ON THE NITRATE ION CONCENTRATION FOR THE ETHYLMALONIC ACID OXIDATION[a]

	$[NO_3^-]$, M	$k_{obs.}$, sec^{-1}	$k_{H,N}$, $M^{-1}sec^{-1}$	$1/k_{H,N}$, M sec
$[H^+]$ = 2.0 M				
	2.60	0.924	46.2	0.0266
	3.60	0.630	31.5	0.0318
	4.60	0.433	21.6	0.0462
	5.60	0.385	19.2	0.0520
	6.60	0.346	17.3	0.0578
$[H^+]$ = 4.0 M				
	2.60	0.495	24.8	0.0404
	3.60	0.330	16.5	0.0606
	4.60	0.266	13.3	0.0750
	5.60	0.210	10.5	0.0952
	6.60	0.182	9.10	0.110
$[H^+]$ = 6.0 M				
	2.60	0.408	20.4	0.0490
	3.60	0.277	13.8	0.0722
	4.60	0.213	10.6	0.0938
	5.60	0.173	8.65	0.115
	6.60	0.150	7.50	0.133

a - $[EMH_2]$ = 0.0200 M, [Ag(II)] = 0.0005 M, [Ag(I)] = 0.0100 M, and I = 6.6 M.

TABLE 19

DEPENDENCE OF $k_{H,N}$ ON THE NITRATE ION CONCENTRATION FOR THE DIMETHYLMALONIC ACID OXIDATION

	$[NO_3^-]$, M	$k_{obs.}$, sec^{-1}	$k_{H,N}$, $M^{-1}sec^{-1}$	$1/k_{H,N}$, M sec
$[H^+] = 2.0$ M[a]				
	1.60	12.5	625	0.00160
	2.60	9.24	462	0.00216
	3.60	7.29	364	0.00274
	4.60	5.78	289	0.00346
	5.60	4.78	239	0.00418
	6.60	4.07	204	0.00491
$[H^+] = 4.0$ M[a]				
	1.60	8.15	408	0.00245
	2.60	5.54	277	0.00361
	3.60	3.74	187	0.00535
	4.60	3.01	150	0.00664
	5.60	2.48	124	0.00806
	6.60	2.10	105	0.00952
$[H^+] = 6.0$ M[b]				
	0.600	2.90	1160	0.000862
	1.60	1.10	440	0.00227
	2.60	0.544	218	0.00460
	3.60	0.370	148	0.00676
	4.60	0.276	110	0.00691
	5.60	0.221	88.4	0.0113
	6.60	0.218	87.2	0.0115

a - $[DMMH_2] = 0.0200$ M, $[Ag(II)] = 0.0015$ M $[Ag(I)] = 0.0100$ M, and I = 6.6 M.

b - $[DMMH_2] = 0.00250$ M, $[Ag(II)] = 0.0005$ M, $[Ag(I)] = 0.100$ M, and I = 6.6 M.

TABLE 20

DEPENDENCE OF $k_{H,N}$ ON THE NITRATE ION CONCENTRATION FOR THE DIETHYLMALONIC ACID OXIDATION[a]

$[NO_3^-]$, M	$k_{obs.}$, sec^{-1}	$k_{H,N}$, $M^{-1}sec^{-1}$	$1/k_{H,N}$ x 10^3, M sec
0.600	3.85	1540	0.649
1.60	1.59	636	1.57
2.60	0.942	377	2.65
3.60	0.673	269	3.71
4.60	0.561	224	4.46
5.60	0.432	173	5.79
6.60	0.399	160	6.26

a - $[DEMH_2]$ = 0.00250 M, [Ag(II)] = 0.00050 M,
[Ag(I)] = 0.100 M, $[H^+]$ = 6.0 M, and I = 6.6 M.

MECHANISM AND DISCUSSION

A mechanism consistent with the obtained results is:

$$Ag^{2+} + LH_2 \overset{K_{51}}{\rightleftharpoons} AgLH_2^{2+} \qquad (51)$$

$$AgOH^{+} + LH_2 \overset{K_{52}}{\rightleftharpoons} AgLH^{+} + H_2O \qquad (52)$$

$$AgLH_2^{2+} \xrightarrow{k_{53}} Ag^{+} + LH\cdot + H^{+} \qquad (53)$$

$$AgLH_2^{2+} + H^{+} \xrightarrow{k_{54}} Ag^{+} + LH\cdot + 2H^{+} \qquad (54)$$

$$AgLH^{+} \xrightarrow{k_{55}} Ag^{+} + LH\cdot \qquad (55)$$

where equations 53, 54, and 55 are the rate determining steps. Also necessary in the consideration of the mechanism are the following equilibria:

$$Ag^{2+} + H_2O \overset{K_{56}}{\rightleftharpoons} AgOH^{+} + H^{+} \qquad (56)$$

$$Ag^{2+} + NO_3^{-} \overset{K_{57}}{\rightleftharpoons} AgNO_3^{+} \qquad (57)$$

$$AgLH_2^{2+} \overset{K_{58}}{\rightleftharpoons} AgLH^{+} + H^{+} \qquad (58)$$

The reactive Ag(II) species, the aquated ion, Ag^{2+}, and the first hydrolysis product, $AgOH^{+}$, formed through equation 56, first react with the substrate, LH_2, to give two intermediate complexes, $AgLH_2^{2+}$ and $AgLH^{+}$, respectively (equations 51 and 52), via kinetically indistinguishable pathways (since $K_{51}K_{58} = K_{52}K_{56}$). Electron transfer within $AgLH_2^{2+}$ can occur alone or by acid catalysis (equations 53 and 54, respectively) to produce a free radical, $LH\cdot$, silver (I), and a proton. Electron transfer within $AgLH^{+}$

will result in the same free radical, LH•, and silver (I) (equation 55). These electron transfer reactions are rate determining and their relative importance depends upon the organic substrate. Participation by Ag(III) has been ruled out since at our kinetic conditions the order with respect to silver (II) is unity provided that the [Ag(I)] > 0.005 M.

Appropriate combination of equations 51-58 yields the rate law:

$$\text{rate} = \frac{\{k_{55}K_{51}K_{58} + k_{53}K_{51}[H^+] + k_{54}K_{51}[H^+]^2\}[LH_2][Ag(II)]_T}{[H^+] + K_{51}[H^+][LH_2] + K_{57}[H^+][NO_3^-] + K_{51}K_{58}[LH_2] + K_{56}} \tag{59}$$

(See the appendix for the complete derivation.) Since the reaction is always first order with respect to LH_2, it is reasonable to assume that $K_{51}[H^+][LH_2] + K_{51}K_{58}[LH_2] << [H^+] + K_{57}[H^+][NO_3^-] + K_{56}$ which results in a simplification of equation 59 to

$$\text{rate} = \frac{\{k_{55}K_{51}K_{58} + k_{53}K_{51}[H^+] + k_{54}K_{51}[H^+]^2\}[LH_2][Ag(II)]_T}{[H^+] + K_{57}[H^+][NO_3^-] + K_{56}} \;. \tag{60}$$

The observed rate constant, $k_{obs.}$, and the second order rate constant, $k_{H,N}$, originally defined by equations 46 and 47, respectively, are now given by

$$k_{obs.} = \frac{\{k_{55}K_{51}K_{58} + k_{53}K_{51}[H^+] + k_{54}K_{51}[H^+]^2\}[LH_2]}{[H^+] + K_{57}[H^+][NO_3^-] + K_{56}} \tag{61}$$

and

$$k_{H,N} = \frac{k_{55}K_{51}K_{58} + k_{53}K_{51}[H^+] + k_{54}K_{51}[H^+]^2}{[H^+] + K_{57}[H^+][NO_3^-] + K_{56}} \qquad (62)$$

The literature values of K_{56} and K_{57} are 0.69 and 0.94 M^{-1}, respectively, at 25°C.[10]

Malonic Acid: For the malonic acid oxidation, equations 53 and 54 are the important rate determining steps thereby simplifying equations 61 and 62 to equations 63 and 64, respectively.

$$k_{obs.} = \frac{\{k_{53}K_{51}[H^+] + k_{54}K_{51}[H^+]^2\}[LH_2]}{[H^+] + K_{57}[H^+][NO_3^-] + K_{56}} \qquad (63)$$

$$k_{H,N} = \frac{k_{53}K_{51}[H^+] + k_{54}K_{51}[H^+]^2}{[H^+] + K_{57}[H^+][NO_3^-] + K_{56}} \qquad (64)$$

Since K_{56} is less than about 5% of the sum of $[H^+] + K_{57}[H^+][NO_3^-]$, it can be neglected and equation 64 now becomes

$$k_{H,N} = \frac{k_{53}K_{51}}{1 + K_{57}[NO_3^-]} + \frac{k_{54}K_{51}[H^+]}{1 + K^{57}[NO_3^-]}. \qquad (65)$$

$k_{H,N}$ vs. $[H^+]$ at constant $[NO_3^-]$ is shown in Figure 11. It is linear with slope $k_{54}K_{51}/(1 + K_{57}[NO_3^-])$ and intercept $k_{53}K_{51}/(1 + K_{57}[NO_3^-])$ (A and B, respectively, of equation 48). The NO_3^- dependency can be explicitly obtained at fixed $[H^+]$, by rearrangement of equation 65 to give

$$\frac{1}{k_{H,N}} = \frac{1}{k_{53}K_{51} + k_{54}K_{51}[H^+]} + \frac{K_{57}[NO_3^-]}{k_{53}K_{51} + k_{54}K_{51}[H^+]}. \qquad (66)$$

The plot of $1/k_{H,N}$ vs. $[NO_3^-]$ at various $[H^+]$, shown in Figure 12, is linear with slope $K_{57}/(k_{53}K_{51} + k_{54}K_{51}[H^+])$ and intercept $1/(k_{53}K_{51} + k_{54}K_{51}[H^+])$ (a and b of equation

50).

Methyl- and Ethylmalonic Acids: For the monosubstituted malonic acid derivatives, equations 53 and 55 are the important rate determining steps and equations 61 and 62 are reduced to equations 67 and 68, respectively.

$$k_{obs.} = \frac{\{k_{55}K_{51}K_{58} + k_{53}K_{51}[H^+]\}[LH_2]}{[H^+] + K_{57}[H^+][NO_3^-] + K_{56}} \qquad (67)$$

$$k_{H,N} = \frac{k_{55}K_{51}K_{58} + k_{53}K_{51}[H^+]}{[H^+] + K_{57}[H^+][NO_3^-] + K_{56}} \qquad (68)$$

Rearrangement of equation 68 yields equation 69 which is the linear form at constant $[NO_3^-]$.

$$k_{H,N}\{[H^+] + K_{57}[H^+][NO_3^-] + K_{56}\} = k_{55}K_{51}K_{58} + k_{53}K_{51}[H^+] \qquad (69)$$

The plots of $k_{H,N}\{[H^+] + K_{57}[H^+][NO_3^-] + K_{56}\}$ vs. $[H^+]$, shown in Figures 13 and 14 for MMH_2 and EMH_2, have a slope of $k_{53}K_{51}$ and an intercept of $k_{55}K_{51}K_{58}$. The nitrate ion dependency at fixed $[H^+]$ is obtained by rearrangement of equation 68 to yield equation 70.

$$\frac{1}{k_{H,N}} = \frac{[H^+] + K_{56}}{k_{55}K_{51}K_{58} + k_{53}K_{51}[H^+]} + \frac{K_{57}[H^+][NO_3^-]}{k_{55}K_{51}K_{58} + k_{53}K_{55}[H^+]} \qquad (70)$$

Equation 70 is plotted in Figures 15 and 16 for MMH_2 and EMH_2. Its slope is $K_{57}[H^+]/(k_{55}K_{51}K_{58} + k_{53}K_{51}[H^+])$ and its intercept is $([H^+] + K_{56})/(k_{55}K_{51}K_{58} + k_{53}K_{51}[H^+])$.

Dimethyl- and Diethylmalonic Acids: For the disubstituted malonic acid derivatives, equation 55 is the only important rate determining step thereby reducing equations 61 and 62 to equations 71 and 72, respectively.

$$k_{obs.} = \frac{k_{55}K_{51}K_{58}[LH_2]}{[H^+] + K_{57}[H^+][NO_3^-] + K_{56}} \qquad (71)$$

$$k_{H,N} = \frac{k_{55}K_{51}K_{58}}{[H^+] + K_{57}[H^+][NO_3^-] + K_{56}} \qquad (72)$$

At constant $[NO_3^-]$, equation 72 has the linear form

$$\frac{1}{k_{H,N}} = \frac{K_{56}}{k_{55}K_{51}K_{58}} + \frac{(1 + K_{57}[NO_3^-])[H^+]}{k_{55}K_{51}K_{58}} \qquad (73)$$

Plots of $1/k_{H,N}$ vs. $[H^+]$ are shown in Figures 17 and 18 for $DMMH_2$ and $DEMH_2$ and have slope $(1 + K_{57}[NO_3^-])/k_{55}K_{51}K_{58}$ and intercept $K_{56}/k_{55}K_{51}K_{58}$. Equation 74, obtained by rearrangement of equation 72, is the linear form for the nitrate ion dependency at constant $[H^+]$.

$$\frac{1}{k_{H,N}} = \frac{[H^+] + K_{56}}{k_{55}K_{51}K_{58}} + \frac{K_{57}[H^+][NO_3^-]}{k_{55}K_{51}K_{58}} \qquad (74)$$

It has a slope of $K_{57}[H^+]/k_{55}K_{51}K_{58}$ and an intercept of $([H^+] + K_{56})/k_{55}K_{51}K_{58}$ and is plotted in Figures 19 and 20 for $DMMH_2$ and $DEMH_2$.

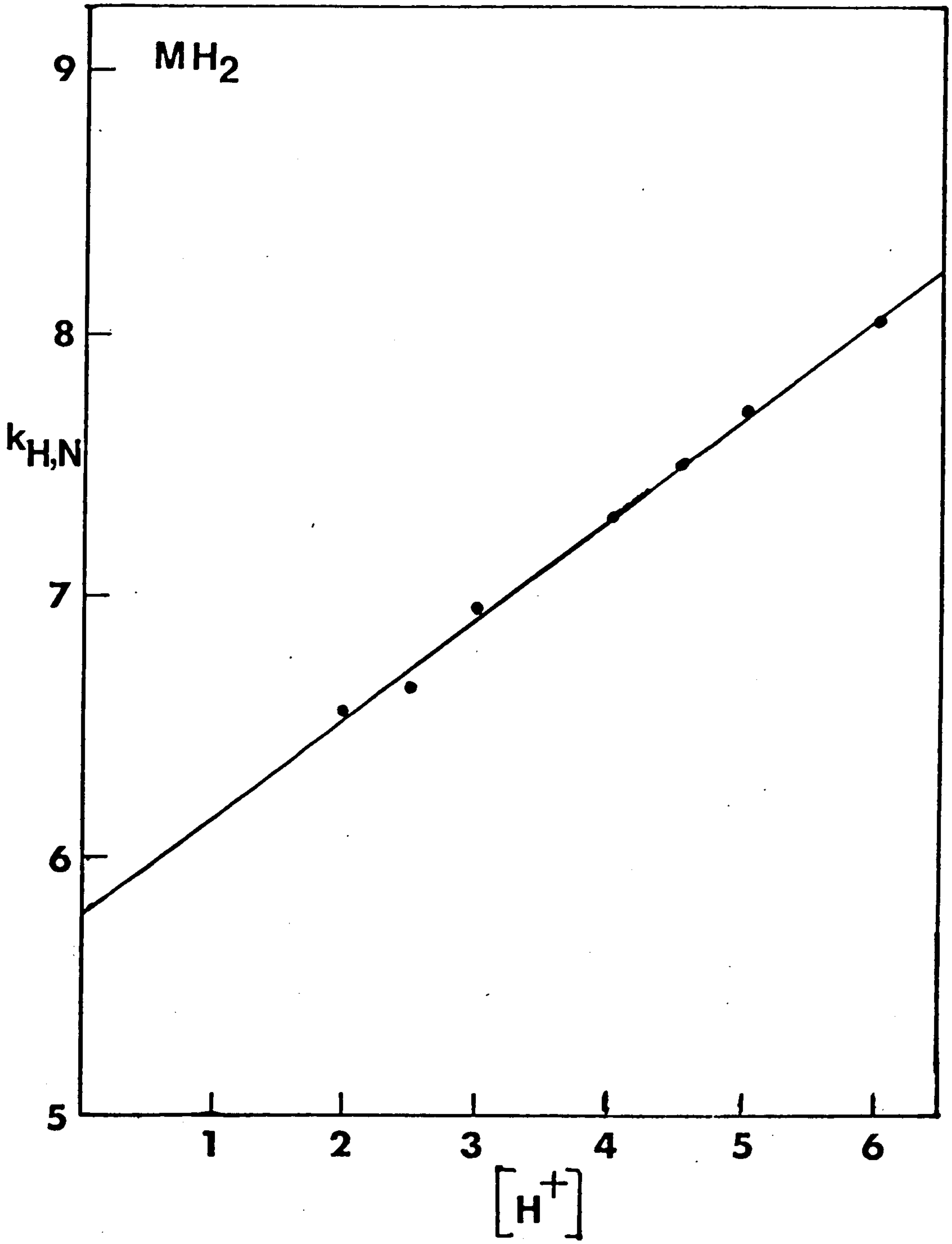
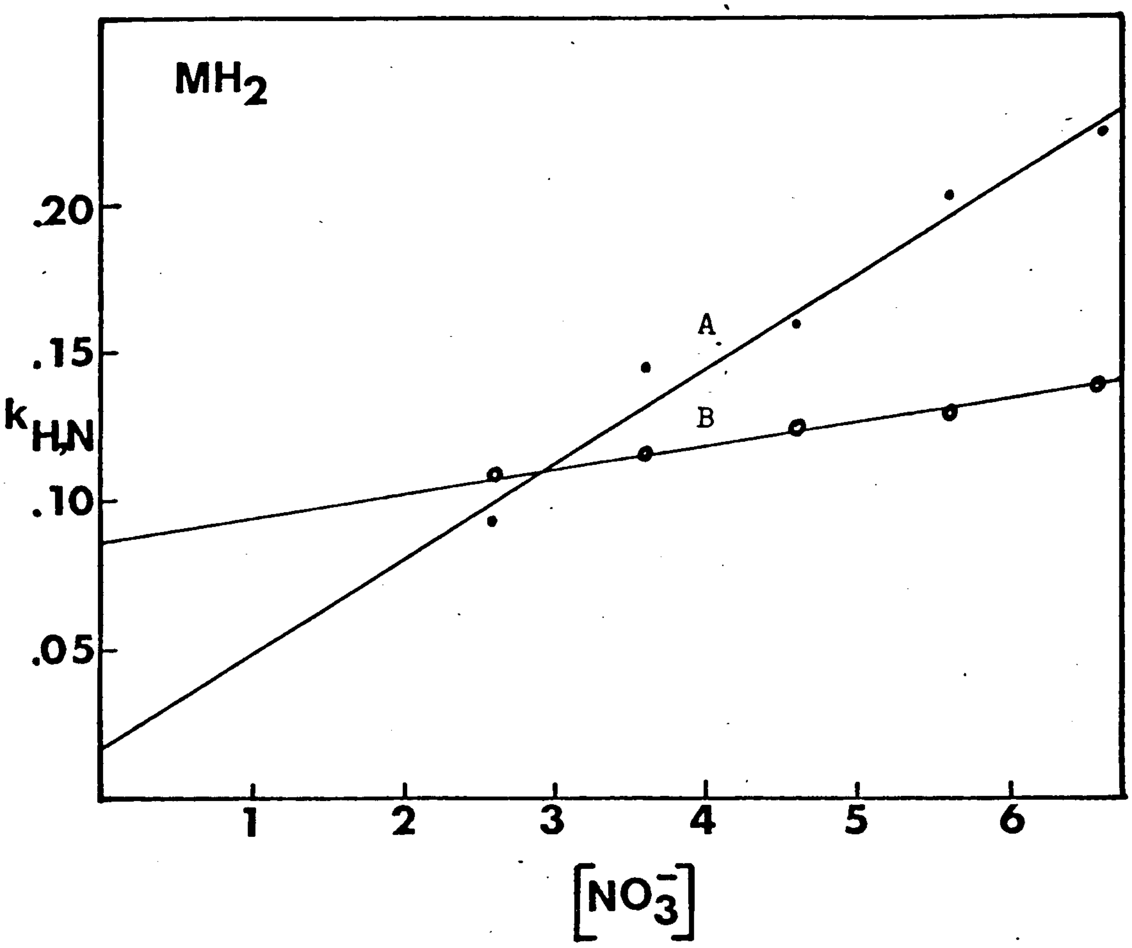


Figure 11. $k_{H,N}$ vs. [H$^+$] for the MH$_2$ oxidation.



A - 2.0 M H^+
B - 6.0 M H^+

Figure 12. $1/k_{H,N}$ vs. $[NO_3^-]$ for the MH_2 oxidation.

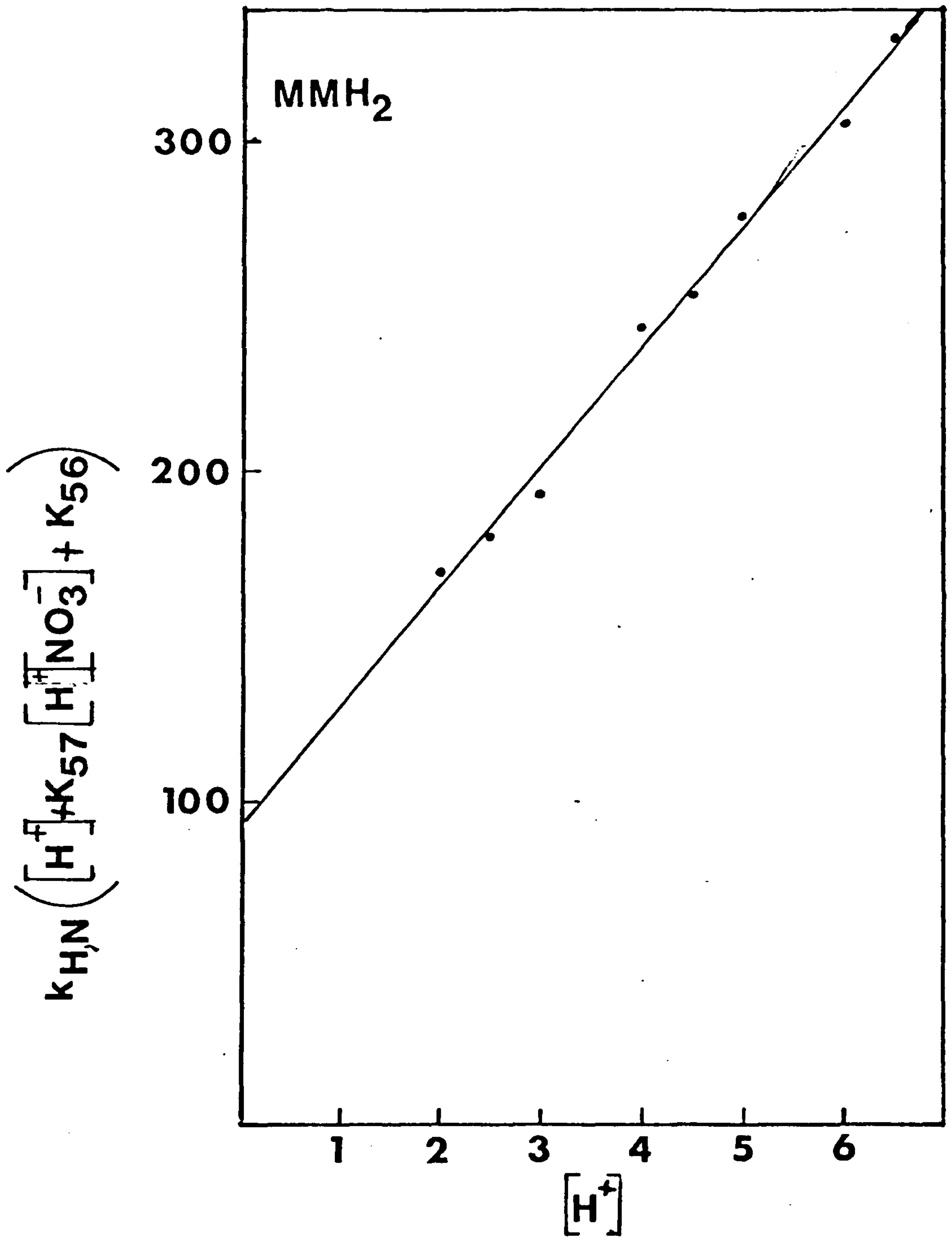


Figure 13. $k_{H,N}\{[H^+] + K_{57}[H^+][NO_3^-] + K_{56}\}$ vs. $[H^+]$ for the MMH$_2$ oxidation.

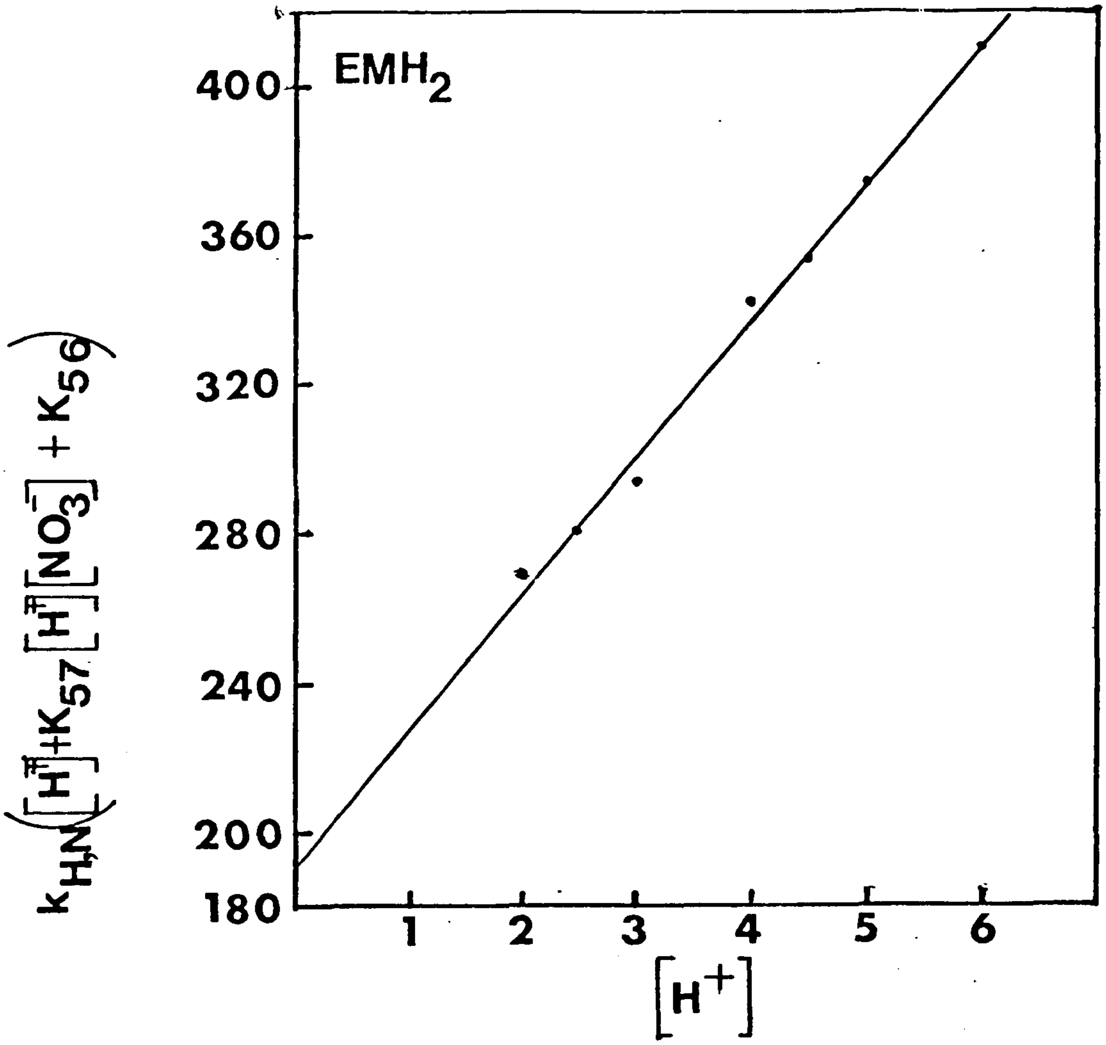
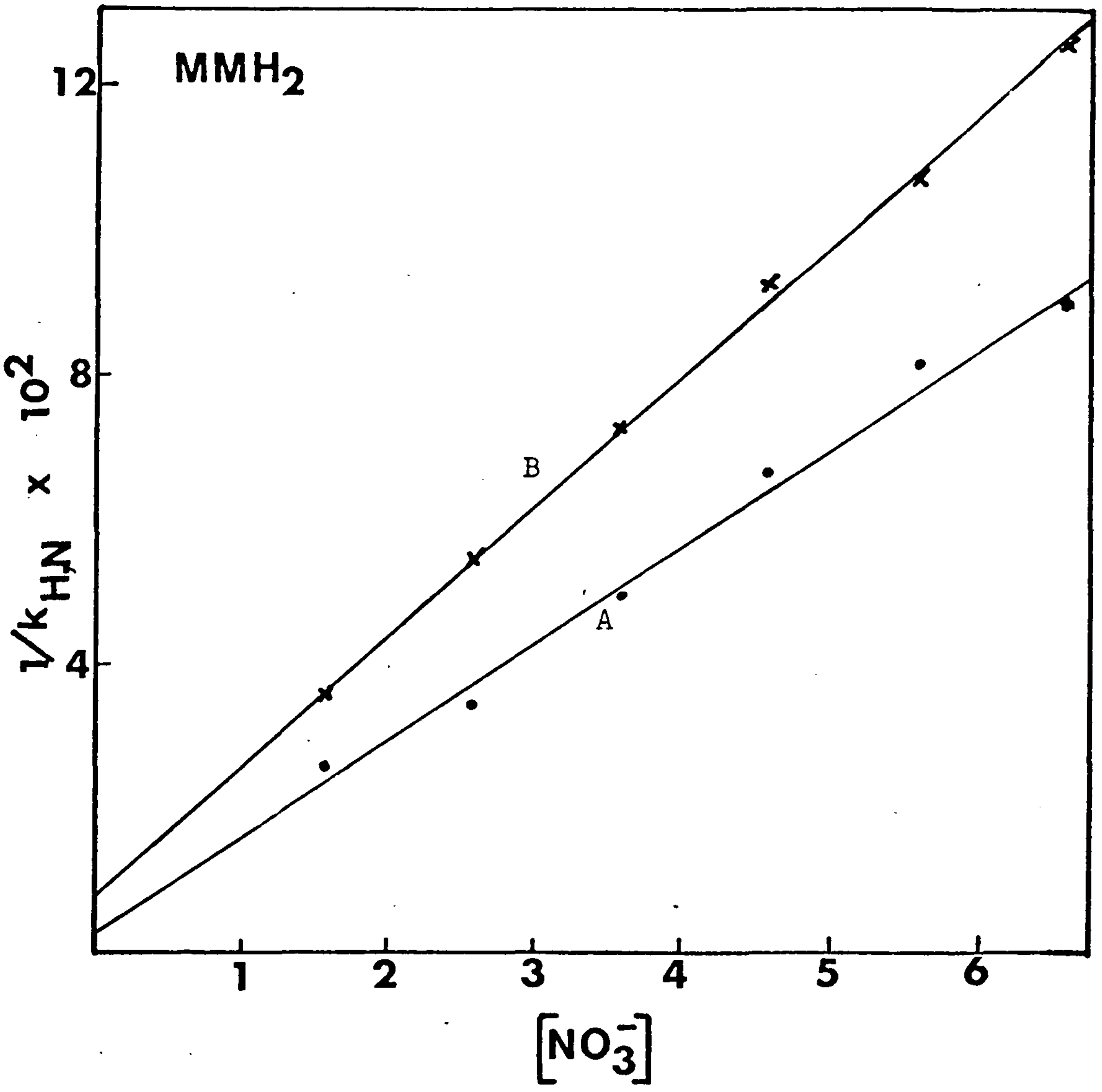
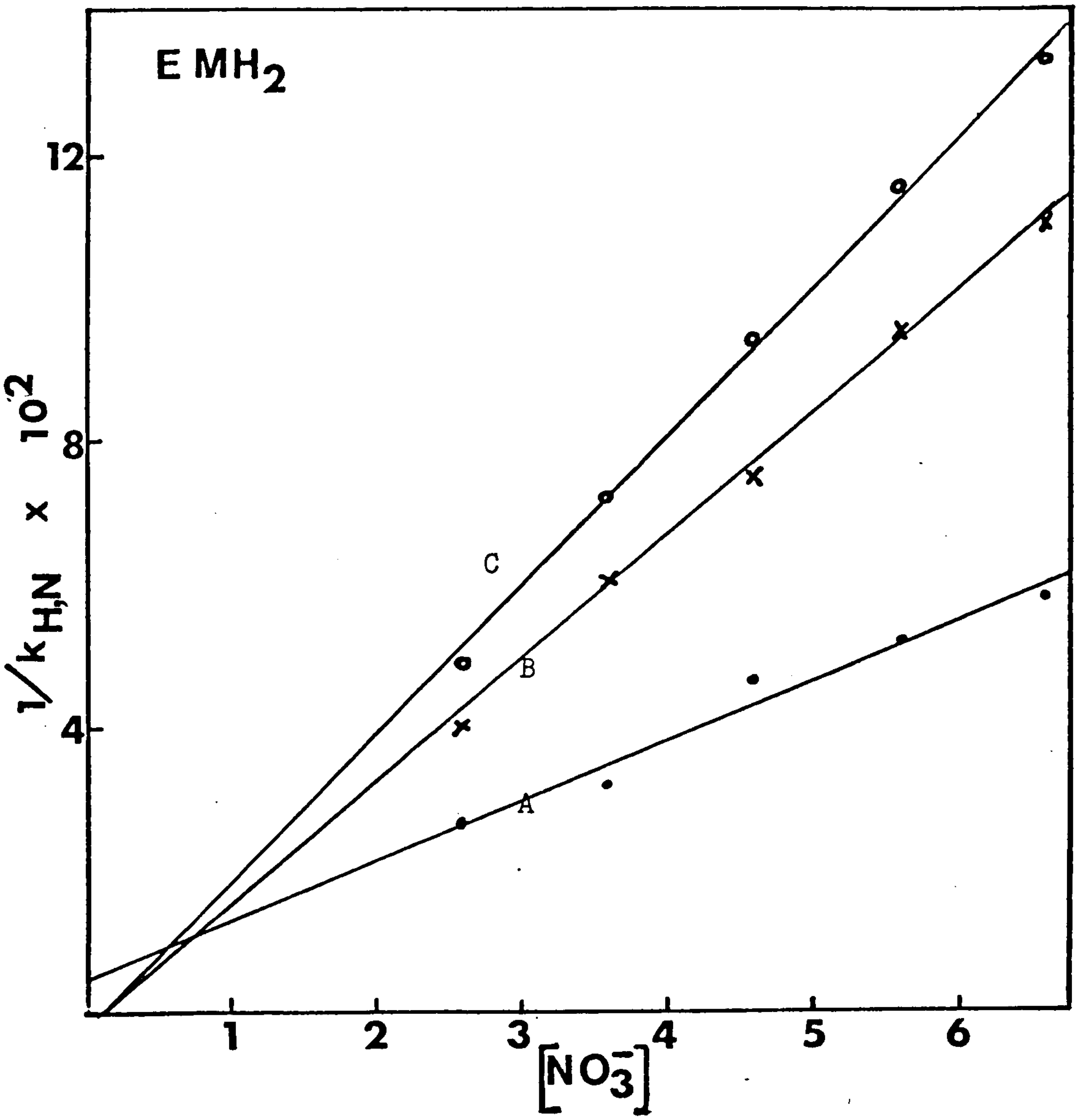


Figure 14. $k_{H,N}\{[H^+] + K_{57}[H^+][NO_3^-] + K_{56}\}$ vs. $[H^+]$ for the EMH_2 oxidation.



A - 2.0 M H^+
B - 4.0 M H^+

Figure 15. $1/k_{H,N}$ vs. [NO_3^-] for the MMH$_2$ oxidation.



A - 2.0 M H$^+$
B - 4.0 M H$^+$
C - 6.0 M H$^+$

Figure 16. $1/k_{H,N}$ vs. [NO$_3^-$] for the EMH$_2$ oxidation.

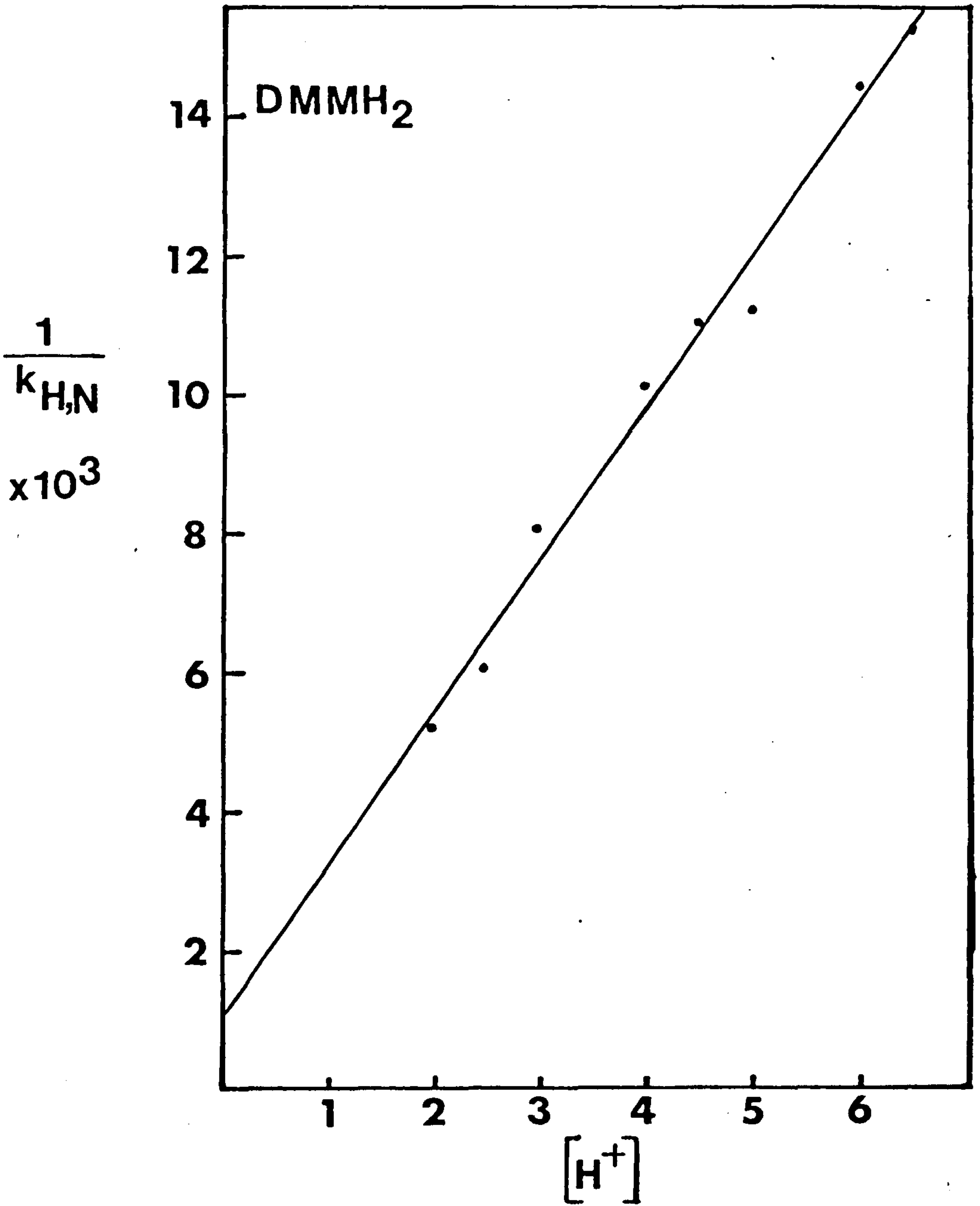


Figure 17. $1/k_{H,N}$ vs. $[H^+]$ for the DMMH$_2$ oxidation.

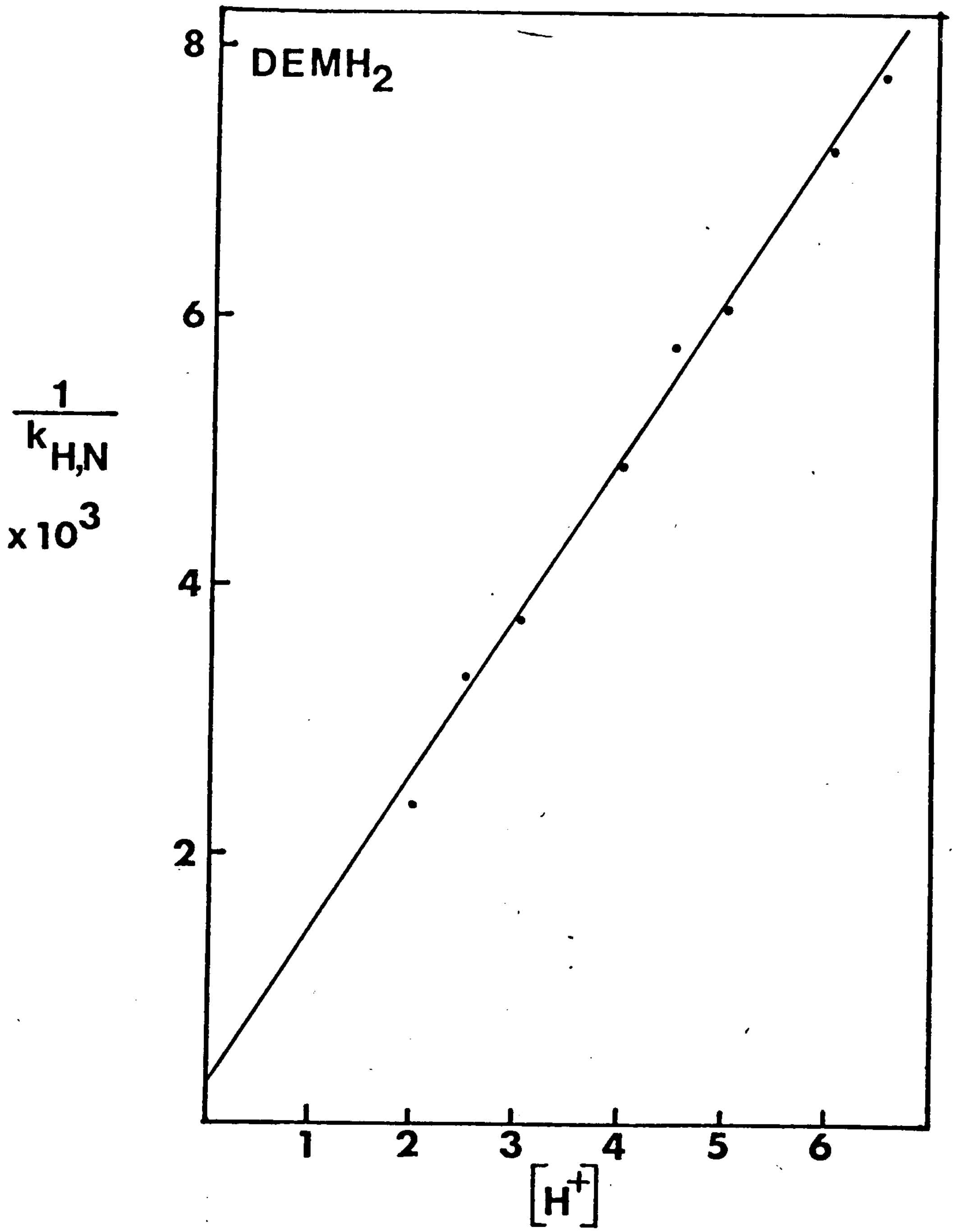
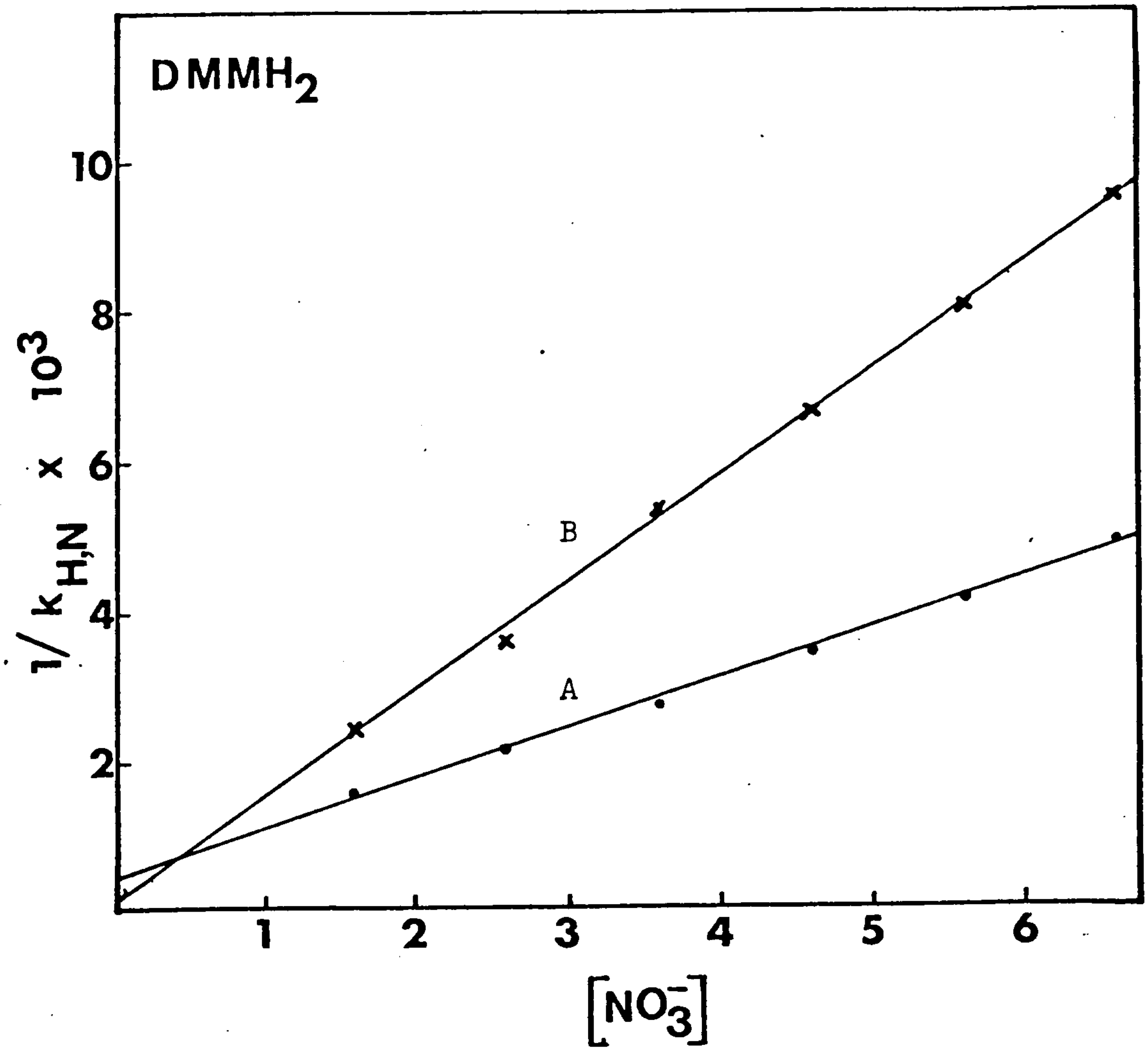


Figure 18. $1/k_{H,N}$ vs. $[H^+]$ for the DEMH$_2$ oxidation.



A - 2.0 M $[H^+]$
B - 4.0 M $[H^+]$

Figure 19. $1/k_{H,N}$ vs. $[NO_3^-]$ for the DMMH$_2$ oxidation.

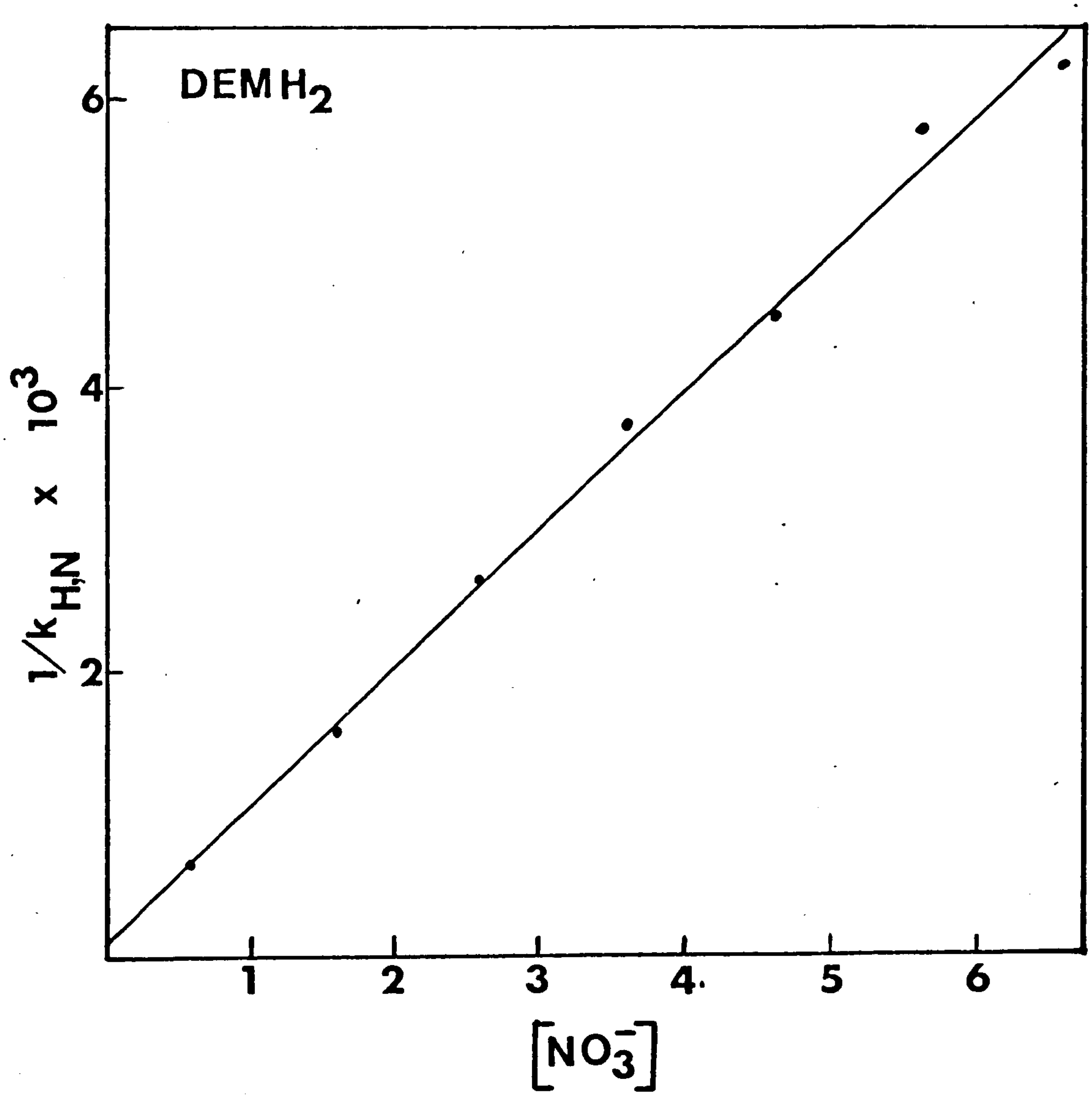


Figure 20. $1/k_{H,N}$ vs. $[NO_3^-]$ for the DEMH$_2$ oxidation.

While individual values of k_{53}, k_{54} and k_{55}cannot be obtained for malonic acid, the relative reactivity, k_{53}/k_{54}, can be obtained by dividing the intercept by the slope (equation 65). The ratio k_{53}/k_{54} is 15 thereby showing that equation 53 is the dominant rate determining step. Unfortunately, the value of k_{53}/k_{55} cannot be obtained because either k_{55} does not contribute or contributes only slightly.

The value of $k_{53}/k_{55}K_{58}$ can be obtained for MMH_2 and EMH_2 as the ratio of the slope to the intercept from Figures 13 and 14, respectively. For MMH_2, this ratio is 0.40 while for EMH_2 it is 0.19. The only generalization that can be drawn is that as the substrate is changed from MH_2 to MMH_2 to EMH_2, the relative importance of the k_{55} rate constant increases at the expense of the k_{53} rate constant. This may in part be due to a larger value of K_{58} for the monosubstituted organic acids. This effect has been observed by McAuley[41] for the α-hydroxycarboxylic acids in which the decomposition of the deprotonated complex predominates.

The values of k_{53}, k_{54}, and k_{55} cannot be determined for the disubstituted derivatives.

The stoichiometry of the reactions of the malonic, methylmalonic, and ethylmalonic acids may be interpreted if the three dicarboxylic acids are oxidized in a series of one-electron steps by Ag(II) to ultimately give formic acid or acetic acid or propionic acid, repectively. This sequence is shown below.

$$\mathrm{Ag(II)} + \mathrm{HCR(COOH)_2} \rightleftharpoons \text{complex} \qquad (75)$$

$$\text{complex} \longrightarrow \mathrm{Ag(I)} + \mathrm{{\bullet}CR(COOH)_2} + \mathrm{H^+} \qquad (76)$$

$$\mathrm{Ag(II)} + \mathrm{H_2O} + \mathrm{{\bullet}CR(COOH)_2} \longrightarrow \mathrm{Ag(I)} + \mathrm{HOCR(COOH)_2} + \mathrm{H^+} \qquad (77)$$

$$\mathrm{HOCR(COOH)_2} + \mathrm{Ag(II)} \longrightarrow \mathrm{O{=}CRCOOH} + \mathrm{{\bullet}CO_2H} + \mathrm{H^+} + \mathrm{Ag(I)} \qquad (78)$$

$$\mathrm{Ag(II)} + \mathrm{{\bullet}CO_2H} \longrightarrow \mathrm{Ag(I)} + \mathrm{CO_2} + \mathrm{H^+} \qquad (79)$$

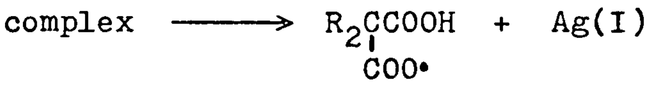
$$\mathrm{Ag(II)} + \mathrm{O{=}CRCOOH} \longrightarrow \mathrm{Ag(I)} + \mathrm{R\underset{\bullet}{C}{=}O} + \mathrm{CO_2} + \mathrm{H^+} \qquad (80)$$

$$\mathrm{Ag(II)} + \mathrm{R\underset{\bullet}{C}{=}O} + \mathrm{H_2O} \longrightarrow \mathrm{Ag(I)} + \mathrm{RCOOH} + \mathrm{H^+} \qquad (81)$$

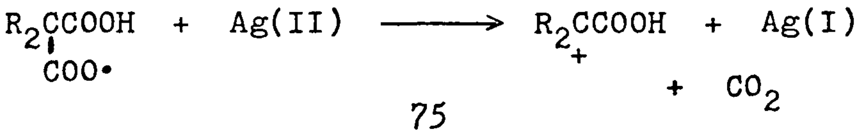
In this sequence, R = H, CH_3-, and C_2H_5-. The anticipated CO_2:Ag(II) mole ratio is therefore 2:6 or 1:3 as was found. The slow step is the decomposition of the complex in which the methylene H must be lost. That the rate determining step involved the loss of this proton was supported by the isotope effect observed using $CD(COOD)_2$ mentioned earlier.

When both methylene H atoms are replaced by either methyl or ethyl groups, as in the disubstituted malonic acid derivatives, there is a significant change in the rate of reaction and a change in stoichiometry. The sequence of reaction for dimethylmalonic acid and diethylmalonic acid is

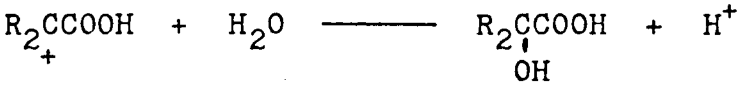
$$\mathrm{R_2C(COOH)_2} + \mathrm{Ag(II)} \rightleftharpoons \text{complex} \qquad (82)$$



$$\text{complex} \longrightarrow \mathrm{R_2\underset{COO\bullet}{\underset{|}{C}}COOH} + \mathrm{Ag(I)} \qquad (83)$$



$$\mathrm{R_2\underset{COO\bullet}{\underset{|}{C}}COOH} + \mathrm{Ag(II)} \longrightarrow \mathrm{R_2\overset{}{\underset{+}{C}}COOH} + \mathrm{Ag(I)} + \mathrm{CO_2} \qquad (84)$$



$$R_2\underset{+}{C}COOH \;+\; H_2O \;\text{———}\; R_2\underset{\substack{|\\ OH}}{C}COOH \;+\; H^+ \qquad (85)$$

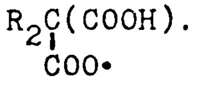
SUMMARY

This study was undertaken to compare the kinetics of the silver (II) oxidation of malonic acid with its mono- and di-, methyl- and ethyl- substituted derivatives. The reaction rates for MH_2, MMH_2, and EMH_2 were found to be similar. The rate of oxidation of $DMMH_2$ was about ten times as fast and that of $DEMH_2$ was about twenty times as fast as for malonic acid.

A mechanism for the oxidations was proposed. The first step is the complexation of the organic acid with the two reactive oxidant species, Ag^{2+} and $AgOH^{+}$, to produce two intermediate complexes, $AgLH_2^{2+}$ and $AgLH^{+}$, which decompose in the rate determining steps to give a free radical, $LH\cdot$, which reacts further. In the case of malonic acid, the important rate determining steps are the uncatalyzed and hydrogen ion catalyzed decompostition of $AgLH_2^{2+}$. In the case of the monosubstituted derivatives, the important rate determining steps are the uncatalyzed decomposition of $AgLH_2^{2+}$ and the decomposition of $AgLH^{+}$. For the disubstituted derivatives, the important rate determining step is the decomposition of $AgLH^{+}$.

The type of free radical formed depends on whether or not there is a methylene hydrogen. If there is a methylene hydrogen, as is the case for MH_2, MMH_2, and EMH_2, it will be abstracted in the rate determining step producing $R\underset{\bullet}{C}(COOH)_2$

where R is CH_3- or C_2H_5-. When there is no methylene hydrogen, as is the case for $DMMH_2$ and $DEMH_2$, the hydrogen which is abstracted in the rate determining step is the one on a carboxyl group. The free radical produced in this instance has the form



$$R_2\underset{\substack{|\\ COO\cdot}}{C}(COOH).$$

These free radicals will undergo a sequence of oxidations to ultimately produce products.

APPENDIX

Derivation of the Rate Law

Since equations 53, 54, and 55 are the rate determining steps, the rate of reaction is represented by

$$\text{rate} = k_{53}[\text{AgLH}_2^{2+}] + k_{54}[\text{AgLH}_2^{2+}][\text{H}^+] + k_{55}[\text{AgLH}^+]. \quad (86)$$

Since $[\text{AgLH}^+] = K_{58}[\text{AgLH}_2^{2+}]/[\text{H}^+]$, from equation 58, the rate equation simplifies to

$$\text{rate} = \{k_{53} + k_{54}[\text{H}^+] + \frac{k_{55}K_{58}}{[\text{H}^+]}\}\ [\text{AgLH}_2^{2+}]. \quad (87)$$

To solve for $[\text{AgLH}_2^{2+}]$ in terms of the total silver (II) concentration, $[\text{Ag(II)}]_T$, the following material balanced equation is used:

$$[\text{Ag(II)}]_T = \text{Ag}^{2+} + \text{AgOH}^+ + \text{AgNO}_3^+ + \text{AgLH}_2^{2+} + \text{AgLH}^+. \quad (88)$$

Rearrangement and combination of equations 51, 56, and 57 to solve for $[\text{Ag}^{2+}]$, $[\text{AgOH}^+]$, and $[\text{AgNO}_3^+]$ in terms of $[\text{AgLH}_2^{2+}]$ yields:

$$[\text{Ag}^{2+}] = \frac{[\text{AgLH}_2^{2+}]}{K_{51}[\text{LH}_2]}, \quad (89)$$

$$[\text{AgOH}^+] = \frac{K_{56}[\text{AgLH}_2^{2+}]}{K_{51}[\text{LH}_2][\text{H}^+]}, \quad (90)$$

and

$$[\text{AgNO}_3^+] = \frac{K_{57}[\text{AgLH}_2^{2+}][\text{NO}_3^-]}{K_{51}[\text{LH}_2]}. \quad (91)$$

Substituting for $[\text{Ag}^{2+}]$, $[\text{AgOH}^+]$, $[\text{AgNO}_3^+]$, and $[\text{AgLH}^+]$ in terms of $[\text{AgLH}_2^{2+}]$ in equation 88 results in the following

$$[\mathrm{Ag(II)}]_T = \frac{[\mathrm{AgLH}_2^{2+}]}{K_{51}[\mathrm{LH}_2]} + \frac{K_{56}[\mathrm{AgLH}_2^{2+}]}{K_{51}[\mathrm{LH}_2][\mathrm{H}^+]} + \frac{K_{57}[\mathrm{AgLH}_2^{2+}][\mathrm{NO}_3^-]}{K_{51}[\mathrm{LH}_2]} + [\mathrm{AgLH}_2^{2+}] + \frac{K_{58}[\mathrm{AgLH}_2^{2+}]}{[\mathrm{H}^+]} . \qquad (92)$$

Solving equation 92 for $[\mathrm{AgLH}_2^{2+}]$ yields

$$[\mathrm{AgLH}_2^{2+}] = \frac{K_{51}[\mathrm{H}^+][\mathrm{LH}_2][\mathrm{Ag(II)}]_T}{\{[\mathrm{H}^+] + K_{56} + K_{57}[\mathrm{H}^+][\mathrm{NO}_3^-] + K_{51}[\mathrm{H}^+][\mathrm{LH}_2] + K_{51}K_{58}[\mathrm{LH}_2]\}} . \qquad (93)$$

Substituting for $[\mathrm{AgLH}_2^{2+}]$ in the original rate expression, equation 87, and rearranging yields the rate law of equation 59 in the text.

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