



A study of the kinetics of the oxidation of maleic hydrazide by ferricyanide in basic aqueous solution
by Robert Baxter Miller

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Chemistry

Montana State University

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Abstract:

Ferricyanide oxidizes maleic hydrazide in aqueous basic solution. The reaction was followed spectrophotometrically by monitoring the disappearance of ferricyanide from the solution. Attempts to study this oxidation without ferrocyanide initially present were unsuccessful due to the speed of the reaction, but when excess ferrocyanide is initially present this reaction follows the following. rate law: [Formula not captured by OCR] This kinetic expression suggests several possible mechanisms which are discussed.

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Signature Robert B. Miller
Date December 19, 1969

A STUDY OF THE KINETICS OF THE OXIDATION OF MALEIC HYDRAZIDE
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by

ROBERT BAXTER MILLER

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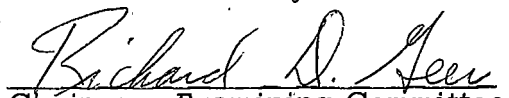
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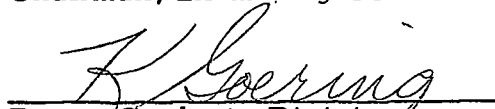
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Abstract

Ferricyanide oxidizes maleic hydrazide in aqueous basic solution. The reaction was followed spectrophotometrically by monitoring the disappearance of ferricyanide from the solution. Attempts to study this oxidation without ferrocyanide initially present were unsuccessful due to the speed of the reaction, but when excess ferrocyanide is initially present this reaction follows the following rate law:

$$-\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = \frac{0.42 [\text{MH}^-]^2 [\text{OH}^-]^2 [\text{Fe}(\text{CN})_6^{3-}]^2}{[0.01 + [\text{MH}^-][\text{OH}^-]] [\text{Fe}(\text{CN})_6^{4-}]^2}$$

This kinetic expression suggests several possible mechanisms which are discussed.

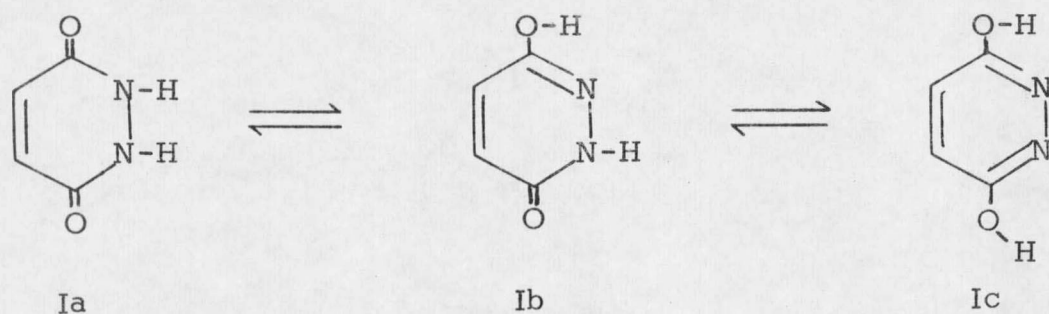
INTRODUCTION

A Partial History of Maleic Hydrazide

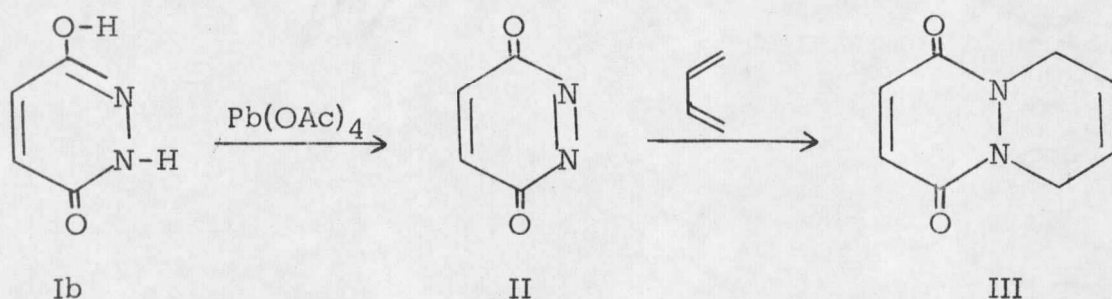
Maleic hydrazide (1,2-dihydro-3,6-pyridazinedione) (I) has been known since 1875¹. It first became of commercial importance when in 1949 Schoene and Hoffman noted that it almost completely inhibited plant growth in tomatoes². It was later found that although it stopped grasses from growing, it did not affect certain other plants such as cotton. This makes it an effective herbicide in mechanized farming.

Because of maleic hydrazide's commercial importance, it has frequently been investigated in a biological environment³. Light, oxidants, and microorganisms in the soil are all known to degrade maleic hydrazide. The object of the present kinetic study of the reaction between ferricyanide, a one-electron abstractor, and maleic hydrazide was to help elucidate the mechanism or mechanisms by which maleic hydrazide is oxidized.

There are three possible tautomeric forms of maleic hydrazide (Ia, Ib, Ic). In 1939 Arndt suggested that the maleic hydrazide molecule exists primarily in the enol form (Ib)⁴. This view was supported by Miller and White's^{5,6} comparative polarographic and ultraviolet study of variously substituted derivatives of maleic hydrazide, and by Ohashi's⁷ and Katritsky's⁸ nuclear magnetic resonance studies.

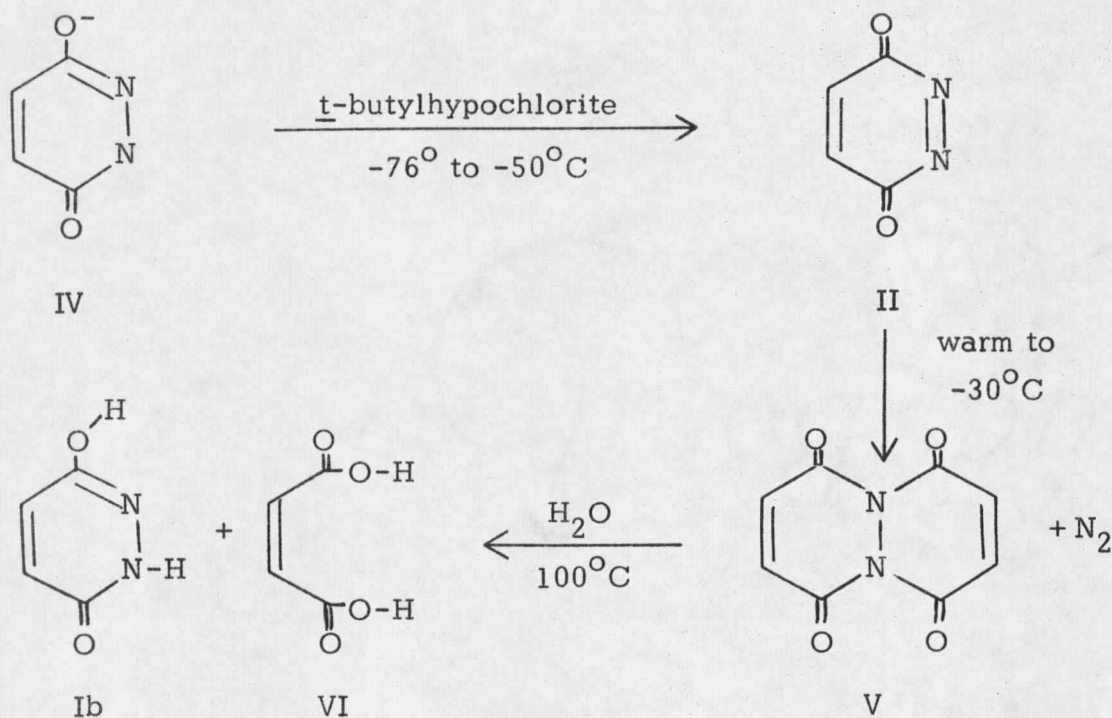


Clement^{9,10} and Kealy¹¹ have both investigated the oxidation of maleic hydrazide. Clement observed that lead tetraacetate oxidized maleic hydrazide in acetone at 0°C. He reported that the reaction mixture turns a slight yellow-green tint and gives off nitrogen. When the reaction was performed with an excess of butadiene in methylene chloride a 76% yield of the Diels-Alder adduct (III) was recovered. Clement concluded from his experiments that the diazoquinone of maleic hydrazide (II) is formed and that it is an excellent dienophile.



Kealy¹¹ used the monoanion of maleic hydrazide in his work. The potassium salt of maleic hydrazide (IV) was oxidized by *t*-butyl hypochlorite in acetone at -50° to -77°C. Kealy found that the emerald

green diazoquinone was stable at -77°C in solution, but dimerized upon warming to form 1,4,6,9-tetraketopyridazino-(1,2-a)-pyridazine (V) (43% yield) at 30°C . In boiling water this product decomposes to maleic hydrazide and maleic acid (VI).



He found that conjugated dienes (butadiene, 2,3-dimethylbutadiene, cyclopentadiene, cyclohexadiene, and coumalic acid) react very rapidly with the diazoquinone at -77°C in isolable yields of approximately 50%. About 6% of the product from all of the diazoquinone reactions was due to the attack of water, which is present in reagent grade acetone, to give maleic anhydride (VIII) and a dimer (VII).

