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SUBJECT: On the Kinetics of Oxidation by Nitric Acid

TO: F. L. Culler

FROM: J. E. Savolainen

ABSTRACT

A method of predicting the oxidation rates by nitric acid in aqueous solutions is indicated by the results of experiments on the ferrous nitroso clock reaction.

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DISCLAIMER

ON THE KINETICS OF OXIDATION BY NITRIC ACID

Nitric acid and ferrous ions in aqueous solution undergo a readily observable clock reaction. On mixing together two solutions, one of nitric acid and the other of ferrous sulfate, in the proper porportions the resultant solution will start to darken after a period of time and then continue to increase in color intensity with an increasing rate. Very shortly after reaching the maximum color intensity the solution will turn abruptly colorless. The color is that of the ferrous nitroso complex of the familiar brown ring test for nitrates and nitrates. The results of the experiments described below show this phenomena may be used as an indicator in the study of the kinetics of oxidation by nitric acid.

An overall reaction between ferrous ions and nitric acid may be written as:

$$3\,Fe^{+2} + 4H^{+} + NO_3^{-} \longrightarrow 3\,Fe^{+3} + 2H_2O + NO. \qquad (1.)$$

The nitric oxide product of the reaction presumably takes part in the equilibrium reaction with unreacted ferrous ion to form the highly colored ferrous nitroso complex:

$$Fe^{+2} + NO \rightleftharpoons (FeNO)^{+2} \qquad (2.)$$

In the early stages of the reaction between ferrous ions and nitric acid the amount of nitric oxide produced by the first reaction (1.) may be determined by the intensity of the color of the complex formed by the second reaction (2). This color would be expected to reach its greatest intensity when the stoichiometry of the composite reaction is reached.

$$4\,Fe^{+2} + 4H^{+} + NO_3^{-} \longrightarrow 3\,Fe^{+3} + 2H_2O + (FeNO)^{+2} \qquad (3)$$

After this point is reached the color diminishes rapidly as the oxidation of the ferrous ion is completed. The time interval from the initial mixing of the solutions to the final disappearance of the color may be assumed to be an inverse measure of the rate of the complete oxidation reaction.

A plot of the logarithm of the time interval as a function of the logarithm of the nitric acid concentration is shown in figure 1. Curve a is the plot of results obtained with nitric acid containing decomposition products as was evident by its yellow color. The position of curve a indicates more rapid reactions, or shorter reaction times, than that of curve b which is plotted from results obtained with nitric acid that had been boiled to remove the lower oxides of nitrogen. Curve c is the plot of results obtained with solutions which contained 0.05 M $(NH_2)_2CO$. The presence of the urea impedes the oxidation reactions. The results displayed in figure 1 indicate that time measurements of the ferrous nitroso clock reaction can be used to estimate the rate at which nitric

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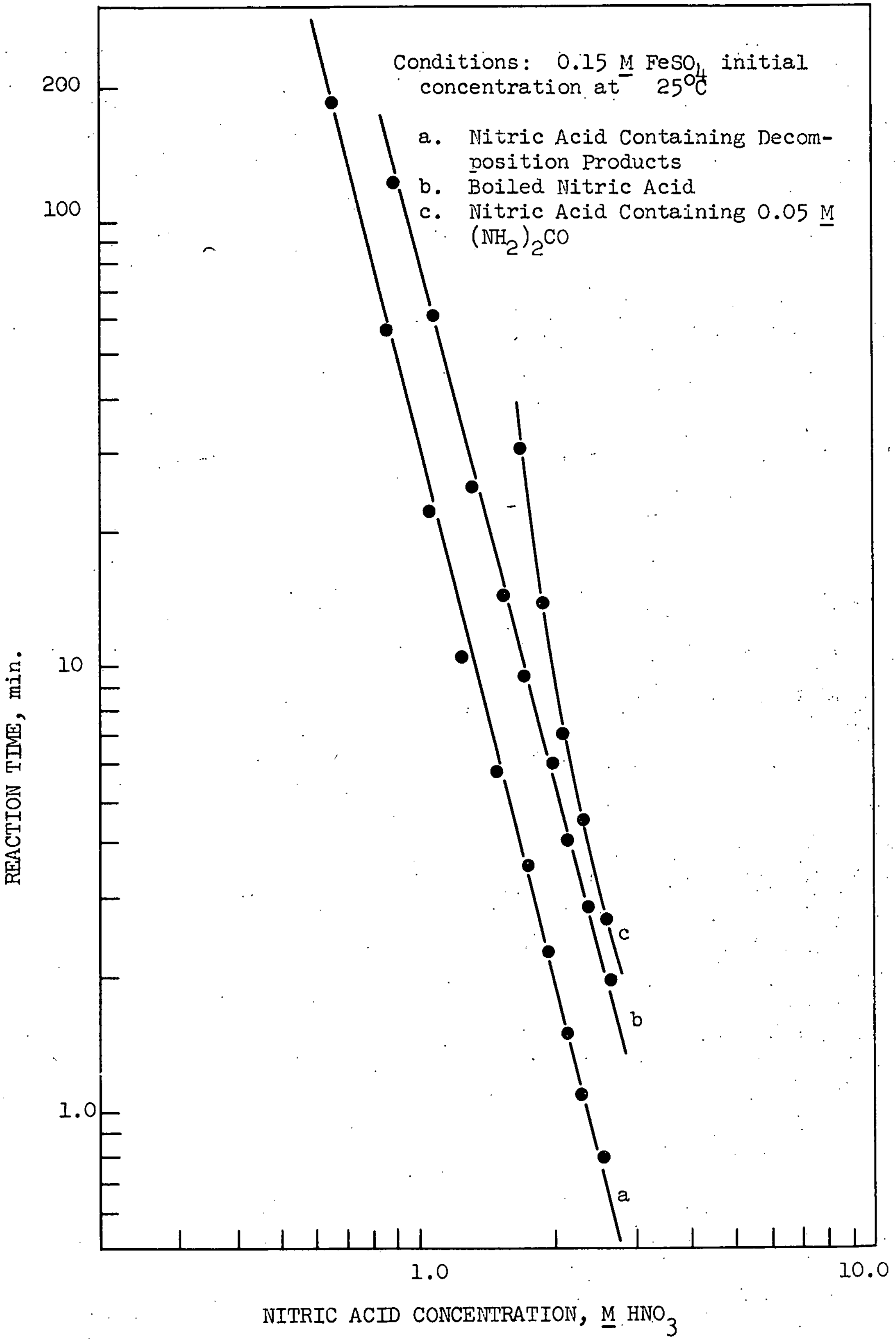

Fig. 1. The Ferrous Nitroso Clock Reaction

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acid solutions may bring about oxidizing reactions and that the reaction rates are predictable.

Some time ago I suggested the ferrous nitroso clock reaction as a problem for undergraduate study to Dr. John G. Surak of Marguette University. Dr. Surak assigned the problem to Duane R. Kobs who obtained the results plotted in figure 2. The results were obtained in the temperature range from 5 to 50°C. and can be described by the expression;

$$a - b \log (\underline{M}\ HNO_3) = \log (\text{Time, min.}),$$

in which "a" and "b" vary with the temperature in a regular manner as is seen in the table below:

Temp° C	a	b
5	2.75	3.52
10	2.35	3.50
20	1.87	3.32
25*	1.80*	3.62*
30	1.50	3.26
40	0.96	3.18
50	0.68	3.14

* from data on plot 2, Fig. 1

The Arrehnius plot of the results obtained by Kobs at 1.838 $\underline{M}$ HNO_3 concentration is shown in figure 3. The activation energy for the over all reaction as calculated from the slope of the plot is 18.4 kcal/mole. This approach to the oxidation kinetics by nitric acid is a simplification of the complicated autocatalytic reaction.

The ferrous nitroso complex has light absorption peaks at 5875 and 4500A°. Below 4500A° the absorption was so intense as to appear continuous and was not resolved. The autocatalytic nature of the oxidation reaction is shown by a time trace of the optical density at 5875A° of a reacting mixture in figure 4. The time trace curve shows that the formation of the ferrous nitroso complex increases at an increasing rate once the reaction has started. The complex under the conditions of the experiment disappears rapidly after reaching its maximum concentration. The concentrations of about one tenth molar ferrous sulfate and from three to four molar nitric acid were used to give results within the limits of the instrument but were not determined exactly. The nitric acid was present in excess as in all experiments. The temperature was not controlled in the absorption cell but the temperature was about 25°C. R. H. Busey of the Chemistry Division recorded the curve with a Carey spectrophotometer.

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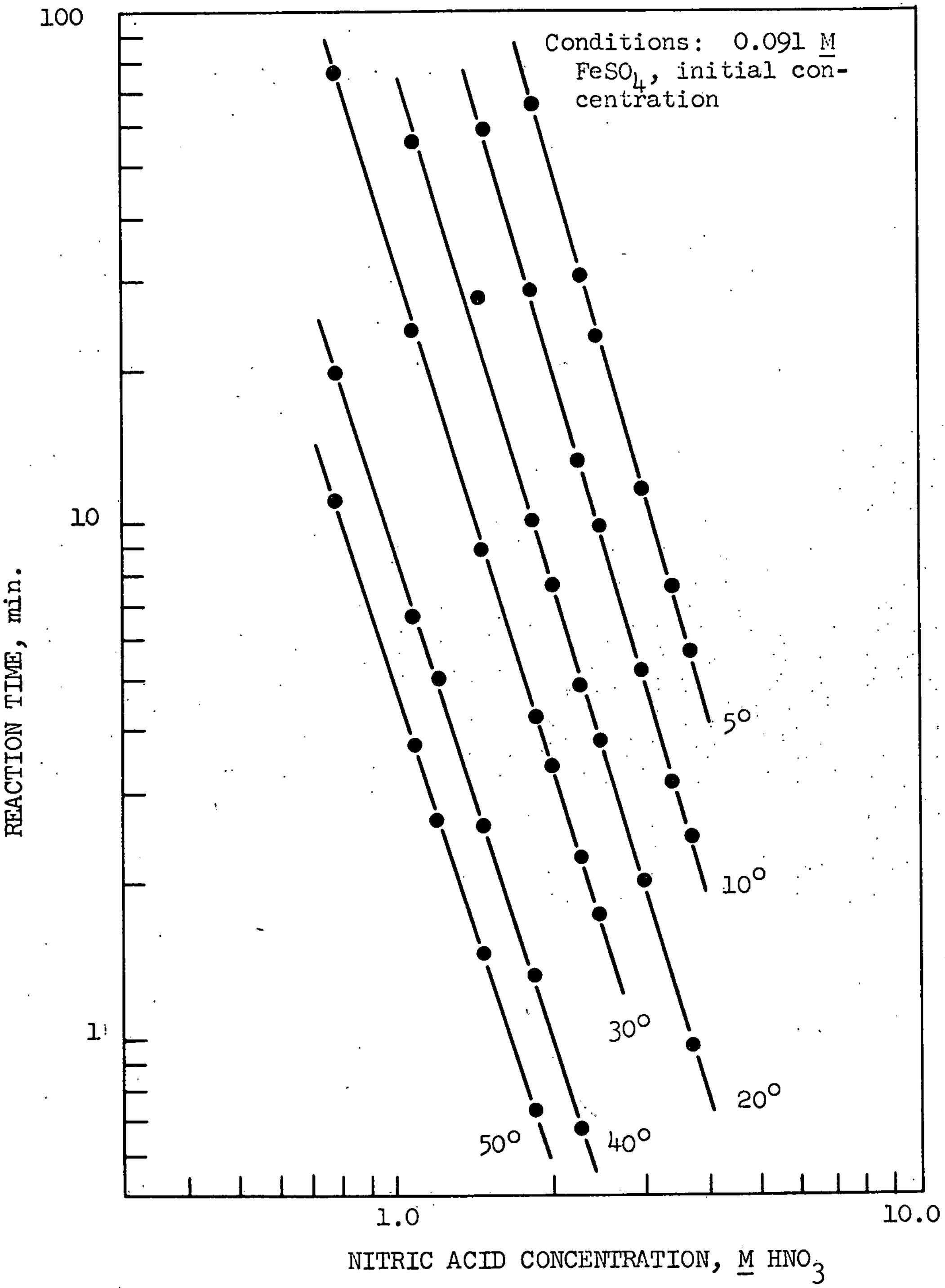

Fig. 2. Ferrous Nitroso Clock Reaction Data from Duane R. Kobs

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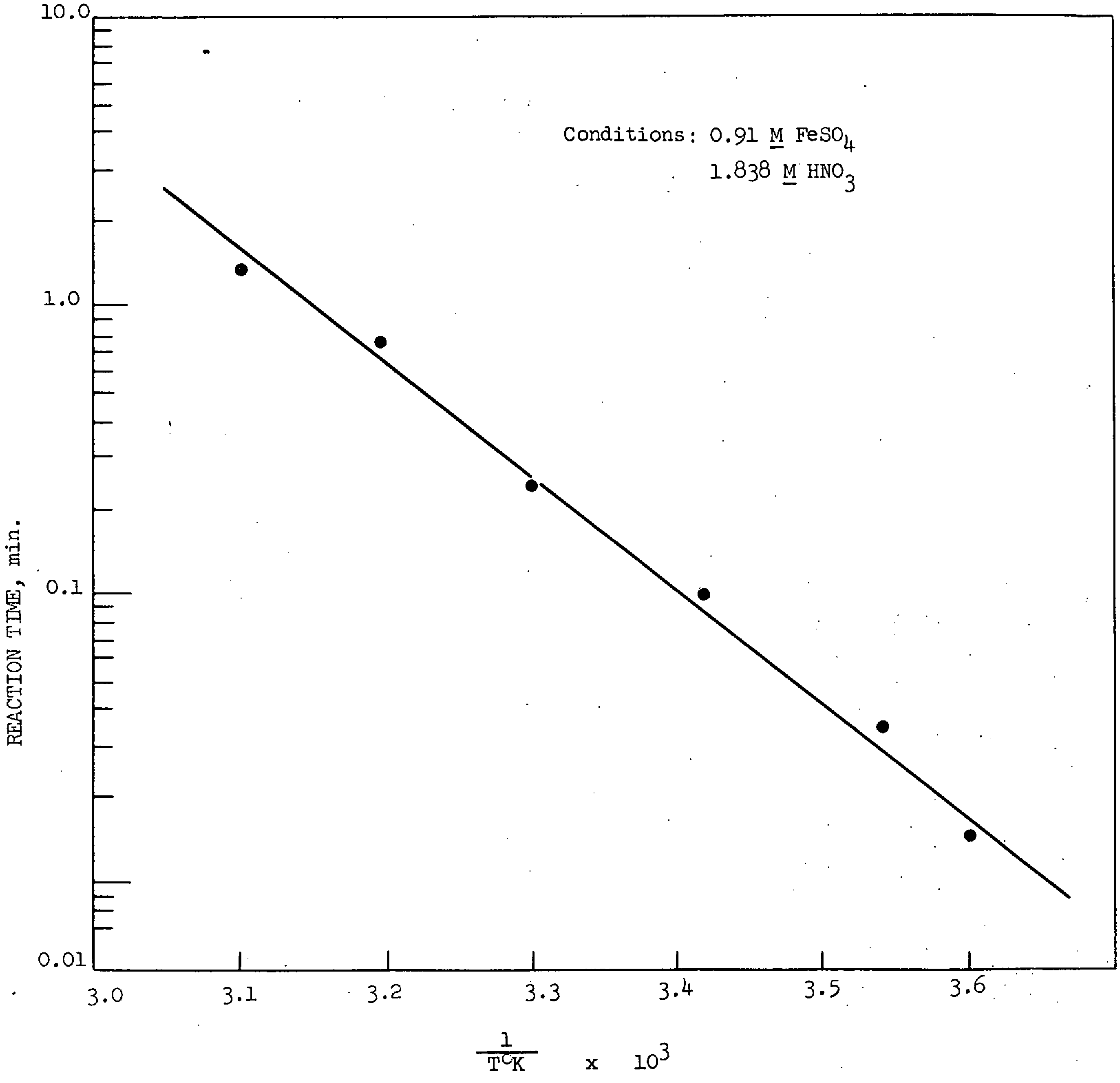

Fig. 3. Arrehnius Plot of the Ferrous Nitroso Clock Reaction.

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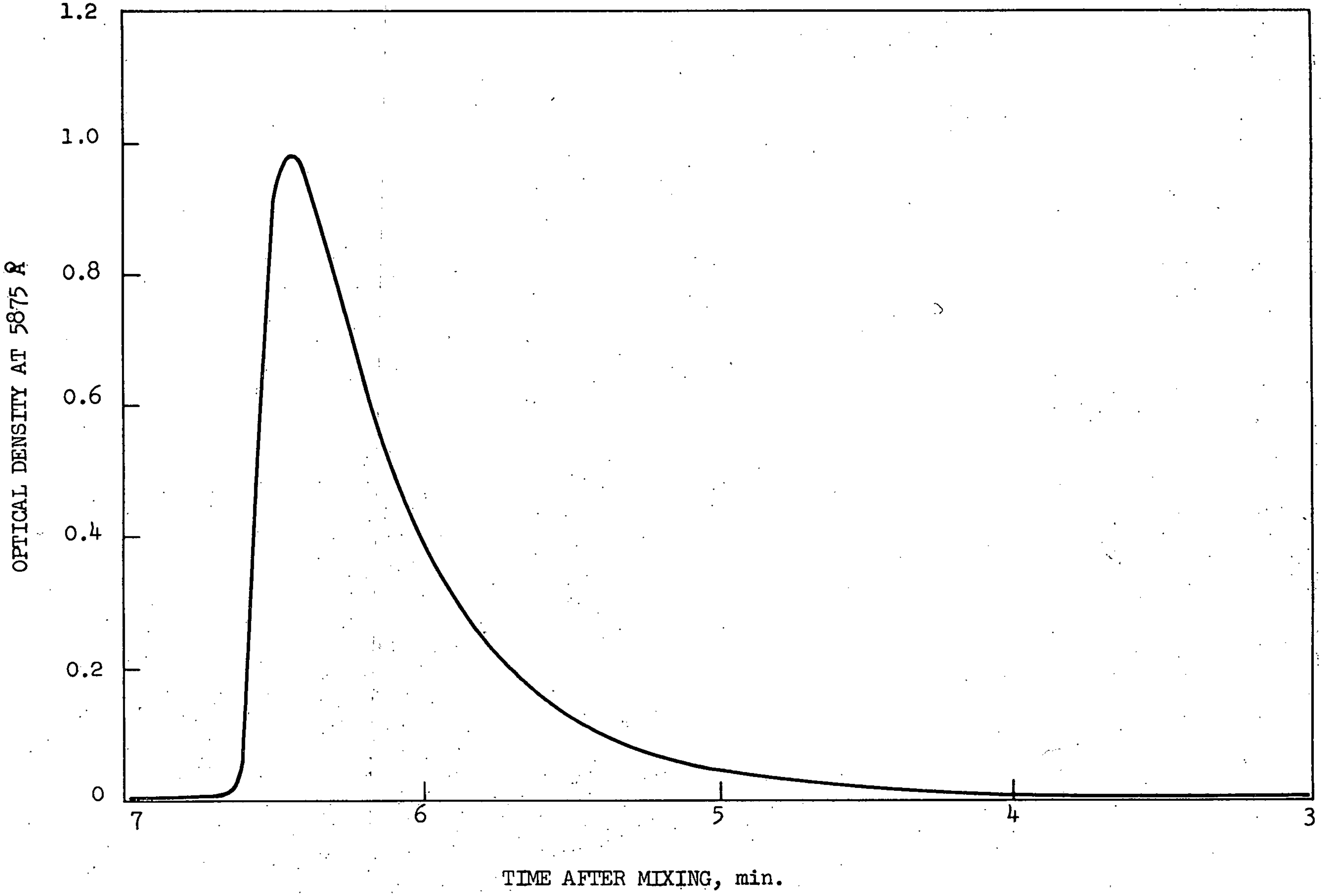

Fig. 4. The Ferrous Nitroso Clock Reaction.

These results indicate that the oxidizing reaction rates by nitric acid are autocatalytic and may be controlled by controlling the temperature and concentrations and by substances which destory the lower oxides of nitrogen.

A clearer understanding of the kinetics of these reactions may be of value in advancing developments in such areas as (1) Oxidation of chlorides to volatile chlorine in the Darex process, (2) Control of oxidation states in solvent extraction columns, (3) Control of contamination in solvent extraction influenced by nitroso complexes, and (4) may be used to indicate radiolysis reactions in aqueous systems.

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