

(where $\Delta/\Delta t_0$ represents the initial velocity) if $[\text{Fe}^{2+}]$ is small in relation to $[\text{HDipy}^+]$. At higher concentrations of ferrous ions, an increase of these is not accompanied, however, by a proportional increase in velocity; on the contrary, after having reached a maximum value, the velocity decreases with a further increase of concentration of ferrous ions. Assuming that this behaviour is due to a rapid formation of an intermediate FeDipy^{2+} which reduces the available concentrations of Fe^{2+} and HDipy^+ (and increases the concentration of hydrogen ions), it is possible to represent the kinetics within the experimental error of ± 10 per cent over a wide range of concentrations, especially with regard to the peculiar dependence on the concentration of ferrous ions, as shown in the table.

$[\text{Fe}^{2+}]$	1.37	5.5	55	165	555×10^{-5}
% found	18.5	69	355	285	$105 \times 10^{-7} \text{ min.}^{-1}$
% calcul.	18.7	68	331	310	$107 \times 10^{-7} \text{ min.}^{-1}$
$[\text{HD}^+] = 1.66 \times 10^{-4}$, $[\text{H}^+] = 1.60 \times 10^{-3}$, $T = 25^\circ$, $\mu = 0.33$					

The values of the constants at 25° and $\mu = 0.33$ are $k_{f_0} = 2.7 \times 10^{15} \text{ min.}^{-1}$ and $k_{f_1} = 1.75 \times 10^{12} \text{ min.}^{-1}$, using the values $K_a = 3.7 \times 10^{-5}$ for the dissociation constant of HDipy^+ and $K_{\text{FeDipy}} = 2.7 \times 10^4$ for the equilibrium constant of FeDipy^{2+} . At $\mu = 0.01$ and $K_a = 4.65 \times 10^{-5}$, K_{f_0} is about 1.7×10^{15} .

If FeDipy_2^{2+} is assumed to be the sole stationary intermediate, it is not possible to represent the kinetics in a satisfactory manner. It is, however, possible to regard FeDipy_2^{2+} as second intermediate, but only if its stationary concentration is small in comparison with the concentration of FeDipy^{2+} . This assumption is even probable on account of the form of the second term of the velocity equation.

The final, rate-determining steps would then be



The overall velocity constant is, within the experimental error, independent of the temperature, K_{FeDipy} showing a small negative temperature coefficient.

The equilibrium constant

$$K = \frac{[\text{FeDipy}_3^{2+}]}{[\text{Fe}^{2+}][\text{Dipy}]^3} = \frac{[\text{FeDipy}_3^{2+}]}{[\text{Fe}^{2+}][\text{HDipy}^+]^3} \cdot \left(\frac{[\text{H}^+] + K_a}{K_a} \right)^3$$

is fairly constant only if $[\text{Fe}^{2+}] < [\text{HDipy}^+]$. With a correction, however, for the formation of FeDipy^{2+} , using the kinetic value of $K_{\text{FeDipy}} = 2.7 \times 10^4$, K remains constant over a very wide range of concentrations, even when the uncorrected value is so low as $K/100$.

The average value of the equilibrium constant at 25° and $\mu = 0.33$ is $K = 3.8 \times 10^{17}$, decreasing to about 2.5×10^{17} at $\mu = 0.01$. The kinetic value of K calculated as the coefficient of the velocity constants of the opposed reactions is 3.6×10^{17} , in excellent numerical agreement with the value directly found.

The heat of formation of FeDipy_3^{2+} at 25° is about 28 kcal. Thus the velocity constant k_{f_0} should have a small positive temperature coefficient (of less than 10 per cent per degree).

We shall try to find further confirmation of the existence of intermediates by investigating the kinetics in neutral solutions and by other methods.

A full account of this work will be published elsewhere.

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Jan. 6.

Baxendale, J. H., and George, P., *Nature*, **163**, 777 (1948); see also Kolthoff, I. M., Lee, T. S., and Leusing, D. L., *Anal. Chem.*, **20**, 985 (1948), on the analogous reaction with *o*-phenanthroline.

THE value of K_{FeDipy} obtained by Dr. Krumholz from kinetic measurements agrees very well with a value of 1.64×10^4 (independent of temperature) which we have obtained from equilibrium measurements based on the incomplete formation of $\text{Fe}(\text{Dipy})_3^{2+}$ in excess ferrous ion reported earlier. It appears from our results that it is not possible to obtain appreciable amounts of $\text{Fe}(\text{Dipy})_2^{2+}$; hence a precise value of K_{FeDipy_2} cannot be obtained, but only its upper limit, $K_{\text{FeDipy}_2} \gtrsim 10^5$.

Over the pH range 0–2.5, our results on the dissociation of $\text{Fe}(\text{Dipy})_3^{2+}$ in hydrochloric acid solution agree with those of Dr. Krumholz, although we believe that the simple explanation involving the formation of the intermediate $\text{Fe}(\text{Dipy})_3\text{H}^{3+}$ is insufficient to explain the following observations. First, the first-order dissociation-rate constants at 35°C . depend on the acid used, and the differences cannot be accounted for by the differing hydrogen ion activities. Secondly, above 1.0 *N* hydrochloric acid, the rate constants are far below the predicted values based on $\text{Fe}(\text{Dipy})_3\text{H}^{3+}$ formation. For example, at 25° and 35°C ., the maximum first-order constants at high hydrogen ion concentration on this assumption (k_{Dipy_2}) are 8.0×10^{-2} and $33.4 \times 10^{-2} \text{ min.}^{-1}$, whereas our observed values are 4.4×10^{-2} and $21.6 \times 10^{-2} \text{ min.}^{-1}$ independent of the acid concentration. Experiments on dissociation in the presence of high salt concentrations at about 0.2 *N* acid show the rate constants to be little altered, so these effects cannot be attributed to kinetic salt effects.

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A Co-operative Transition in a Mixed Ketone Shown by a Change of Dielectric Constant

In a paper on the dielectric properties of dipolar solids, Fröhlich¹ considers the theory of second-order transitions in long-chain ketones. Starting from the crystal structure of these materials, he shows the possibility of co-operative transitions in the solid, and derives an expression for the behaviour of the dielectric constant at such a transition. This theory is derived for pure ketones; but so far no ketone has been found to show a transition of the type in question, the energy conditions being apparently unfavourable. However, such a transition has now been found in a binary mixture of a ketone and a paraffin, namely, 25 per cent of $\text{C}_6\text{H}_{13}\text{COC}_{11}\text{H}_{23}$ with 75 per cent of $\text{C}_{17}\text{H}_{35}$.

The mixture in question has two phases when in equilibrium, the main component being a solid solu-