Complex formation of Rhodium (III) with 1-phenyl-3-pyrazolidone

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1-Phenyl-3-pyrazolidone (Phenidone) has been widely used in photography as a reducing agent.[1] Now complex formation between Rh^{3+} and phenidone is reported.

On mixing a Rh^{3+} solution in perchloric acid (2M, 4M, 6M) with a solution of phenidone in perchloric acid of the same concentration, at 20°C, a change in colour from light pink to red, brown and finally blue-green is observed and this is attributed to complex formation between Rh^{3+} and phenidone. The time required for its appearance, as well as its intensity and shade, depend on the concentrations of the solutions used. At high concentrations the colour develops in a few minutes, otherwise it requires several hours.

The Rh^{3+} and phenidone solutions (in $HClO_4$) were prepared 0·5h before mixing. The acid concentration,

which was kept constant, defined the ionic strength of the solutions. It was observed that it was not necessary to exclude air since phenidone is oxidised at higher pH values.[2] The formation of the complex is hindered at higher temperatures than 20°C. The absorption spectra of the complex is characterised by a maximum at 598mμ. The solutions of Rh^{3+} and phenidone show no significant absorbance in the range 540–800mμ. The optical density (D) at 598mμ increases with time, reaches a maximum 'plateau value' and then diminishes. For solutions in 2M perchloric acid this plateau is reached after 20h from mixing and extends over ca 7h. For solutions in 4M perchloric acid it was found that 22h and 9h were required, and for solutions in 6M perchloric acid 50h and 30h respectively were needed. All optical density values used for the calculation of the constants correspond to these plateaux.

A second maximum at 563, 556 and 548mμ for the solutions in 2M, 4M, 6M perchloric acid, respectively, appears at the beginning of mixing and disappears at an early stage of colour development.

The ratio between Rh^{3+} and phenidone in the complex was determined by the methods of continuous variations[3] and of Bent and French.[4] The plot of difference in absorbance as a function of the composition has a maximum, and the composition at this point is related to the ratio of the two complexing species in the complex. In the Fig the results of the application of this method to the phenidone-Rh^{3+} system is given. Plots of the increase in absorbance, owing to the complex formation against the composition, gave curves with maxima corresponding to a ratio of phenidone: Rhodium (III), 1:1. Similar results are obtained if the concentration of perchloric acid is changed from 2M to 4M and 6M. In all cases only one complex is formed in the ratio 1:1.

The second method for unstable complexes is based on the relation, $\log A_mB_n = m\log A + n \log B - \log K$ which is obtained by taking the mass action expression.

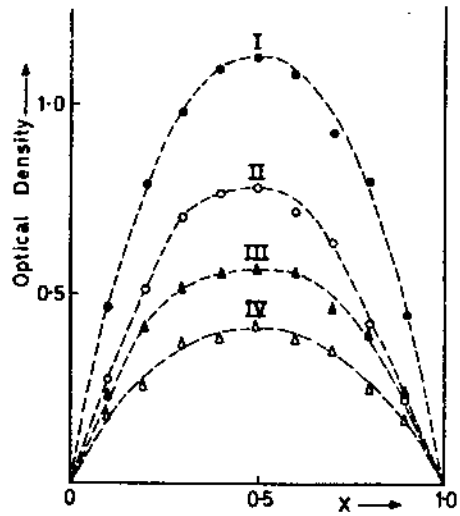

Fig Method of continuous variations. Phenidone: (1-x)0.01M and $RhCl_3$: x0.01M in 2M $HClO_4$ (curves I and III). Phenidone: (1-x)0.003M and $RhCl_3$: x0.008M in 2M $HClO_4$ (curves II and IV). Curves I, II: 598mμ, curves III, IV: 563mμ

From the slopes

$$\left(\frac{d \log D}{d \log A}\right)_B \text{ and } \left(\frac{d \log D}{d \log B}\right)_A$$

it is found that $m = 1$, $n = 1$.

The calculated instability constant was found to be $K = 2{\cdot}4 \times 10^{-2}$, which is independent of $HClO_4$ concentrations used.

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