

Kinetic Studies on the Formation and Decomposition of Bis(peroxo)oxochromium(vi) in Aqueous Solution

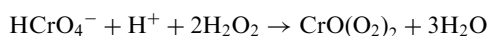
Usama El-Ayaan, Rosmarie Reisacher and Wolfgang Linert*

Institute of Inorganic Chemistry, Technical University of Vienna, Getreidemarkt 9/153, A-1060 Vienna, Austria

The reaction of chromic acid with hydrogen peroxide is studied kinetically and the stability of the product throughout the formation of adducts with donor molecules is investigated.

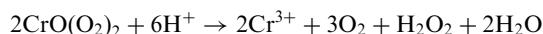
The formation of peroxochromic acid was followed at 580 nm; it quickly decomposes on standing in aqueous solution, but can persist and stabilise in an ether medium. Etheral CrO_5 produces a keto lactone from tetracyclone.¹

The formation reaction of peroxychromium(vi) is assumed to be as follows:



Investigating the order of reaction with respect to the formation shows a first order with respect to the hydrogen peroxide, hydrogen ion and chromium(vi) concentrations with the rate law third order overall.

The decomposition reaction is assumed to be as follows:



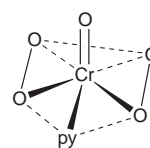
The corresponding rate law is

$$-\text{d}[\text{CrO}_5]/\text{d}t = k_2[\text{CrO}(\text{O}_2)_2][\text{H}^+] + k_3[\text{Cr}(\text{OH})(\text{O}_2)^{2+}][\text{H}^+]$$

which confirms a first order decomposition with respect to hydrogen ion.

The effect of donor molecules on the stability of the blue peroxochromic acid was studied by the addition of pyridine and some other molecules. The presence of pyridine has a marked effect on the rate of decomposition. The stability

is assumed to arise because pyridine is able to form a pentagonal pyramidal compound,² Scheme 2, which was confirmed by its crystal structure.³



(py)CrO(O₂)₂

Scheme 2

The presence of other donor molecules, like dimethyl sulfoxide, dimethylformamide and 2,6-dimethylpyridine, unlike pyridine, showed no effect on the rate of the reaction.

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*To receive any correspondence.