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MECHANISMS OF HALATE-HALIDE REACTIONS

A Thesis presented to the University of Auckland
for the Degree of Doctor of Philosophy

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July 1965

ACKNOWLEDGEMENTS

I am greatly indebted to my supervisor, Dr. G.A. Wright, for inspiration, discussion and suggestion.

The advice and help of my colleagues and the technical staff is sincerely appreciated.

I wish to thank the University Grants Committee for financial assistance in the form of a Research Fund Fellowship (1963) and an Internal Post-Graduate Scholarship (1964-1965).

ABSTRACT

An amperometric method has been developed for continuous determination of iodine concentrations of the order of 10^{-5} molar.

Catalysis of the bromate-iodide and iodate-iodide reactions by carboxylate and phosphate ions has been shown to occur. The rates of these reactions may be expressed:

$$-\frac{d(\text{BrO}_3^-)}{dt} = k_o(\text{H}^+)^2(\text{I}^-)^1(\text{BrO}_3^-)^1 + k_b(\text{B}^-)^1(\text{H}^+)^2(\text{I}^-)^1(\text{BrO}_3^-)^1$$

$$-\frac{d(\text{IO}_3^-)}{dt} = k_o(\text{H}^+)^2(\text{I}^-)^2(\text{IO}_3^-)^1 + \frac{k_b(\text{B}^-)^1(\text{H}^+)^2(\text{I}^-)^2(\text{IO}_3^-)^1}{1 + k'(\text{I}^-)^1}$$

The structure of the iodate ion in solution has been investigated. It has been concluded that the predominant species is the pyramidal IO_3^- ion, and any aquated form is present to the extent of no more than one part in 10^8 .

Previous studies of halate-halide and related reactions have been reviewed, and mechanisms have been postulated for these reactions on the basis of available information.

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