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Chemical Kinetics of KI Catalyzed H_2O_2 Decomposition

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CHEMICAL KINETICS OF KI CATALYZED H_2O_2 DECOMPOSITION

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This research was done to determine the rate constant for the iodide catalyzed decomposition of H_2O_2 and its variation with temperature, so that speculations may be made about the nature of the reaction mechanism.

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Experimentation

Hydrogen peroxide decomposes when catalyzed by the iodide ion as follows:

$$2\ H_2O_2 \xrightarrow{I^-} 2\ H_2O + O_2$$

The rate at which oxygen gas is evolved was measured at various concentrations and temperatures using a buret and a leveling bulb. As the water was forced down the buret by the evolving gas, the leveling bulb was held at the same height while the time required for each ml of gas to be produced was recorded by tracing the path of the second hand of a clock with a pen and making an indentation every ml. The numbers of mls. in an interval of time were counted and the rate (moles/sec) was calculated assuming ideal gas behavior. The rate constant was calculated for each temperature by the following equation, since the reaction was determined to be second order: $k = \text{rate}/(I^-)\ (H_2O_2)$. The values are charted below.

Temp.	*Rate Constant*	*Temp.*	*Rate Constant*
4.0°C	1.82×10^{-5}	24.8	1.72×10^{-4}
6.0	2.22×10^{-5}	25.0	1.78×10^{-4}
7.0	2.33×10^{-5}	26.0	1.12×10^{-4}
12.0	3.45×10^{-5}	26.2	2.01×10^{-4}
13.7	3.98×10^{-5}	26.2	1.31×10^{-4}
20.5	1.45×10^{-4}	26.2	5.14×10^{-4}
21.0	1.26×10^{-4}	26.2	4.05×10^{-5}
21.0	1.10×10^{-4}	26.6	2.33×10^{-4}
21.0	1.04×10^{-4}	25.6	1.22×10^{-4}
23.0	1.29×10^{-4}	26.6	2.77×10^{-4}
23.2	1.36×10^{-4}	32.0	6.21×10^{-5}
24.0	1.35×10^{-4}	36.6	3.64×10^{-4}
24.0	1.38×10^{-4}	37.0	3.57×10^{-4}
24.0	1.36×10^{-4}	39.5	4.50×10^{-4}
24.0	1.64×10^{-4}	40.0	5.82×10^{-4}

Temp.	*Rate Constant*	*Temp.*	*Rate Constant*
43.0	6.00×10^{-4}	58.0	1.82×10^{-3}
43.8	8.33×10^{-4}	63.0	2.30×10^{-3}
48.0	8.40×10^{-4}	73.0	6.65×10^{-3}
49.6	1.31×10^{-3}	73.2	7.15×10^{-3}
58.0	2.99×10^{-3}		

The preceeding data has been plotted on the graph, "k vs. Temp." (Figure 1.) Since the relationship is exponential, the same data was plotted using log values for the rate constant on the graph, "Log_{10} k vs. 1/Temp." The slope of the straight line formed equals 3704 (d log k/d T). From this, the activation energy, E^*, was calculated using the Arrhenius equation, $d \ln k/d T = E^*/RT^2$, and found to equal 17 kcal.

From this information and other theoretical aspects of the reactants, the hypoiodite ion, IO-, was considered as an intermediate complex and the following reaction mechanisms deduced as possibilities:

$$1.\ H_2O_2 + I^- \longrightarrow IO^- + H_2O + H_2O_2 \longrightarrow H_2O + O_2 + I^-$$

$$2.\ 2\,H_2O_2 + 2\,I^- \longrightarrow 2\,IO^- \longrightarrow 2\,I^- + O_2$$

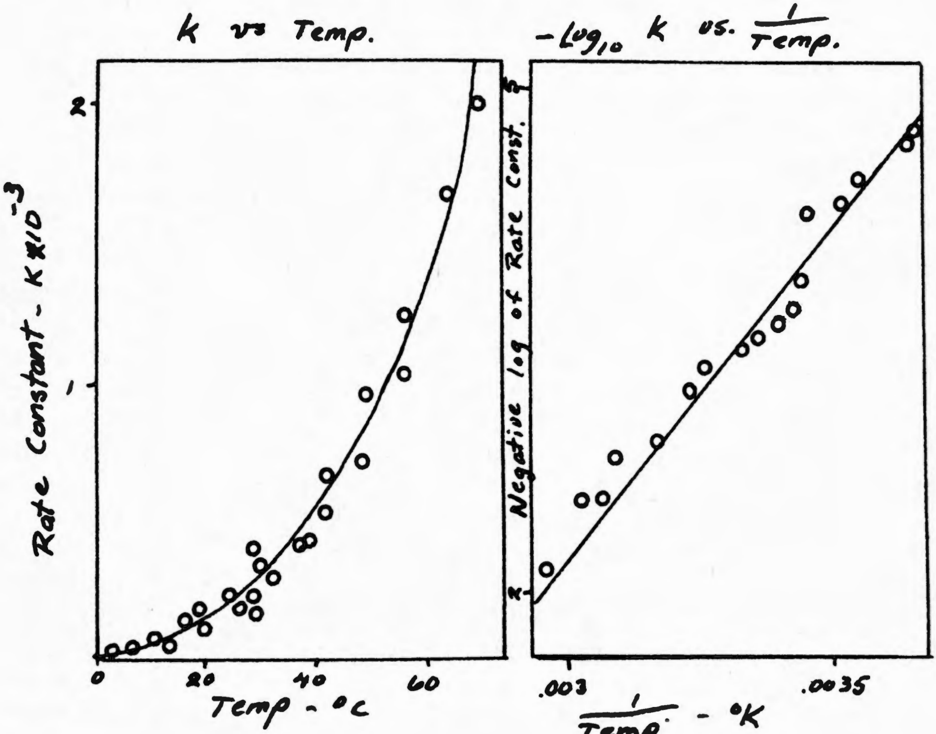

Figure 1

Attempts were made to establish experimentally the IO^- ion as the intermediate complex by spectrographical analysis in the visible light region, since a yellow color resulted when the reacting solutions were mixed. These tests indicated that the color was due to the tri-iodide ion, I_3^-, as shown on the graph of the absorption spectras of the unknown solution and the known tri-iodide solution.

Both graphs, of the known and unknown solutions are parabolic with the point of highest absorption at 6700 A. (Figure 2.) The I_3^- ion is not believed to be the intermediate complex, but rather due to a reaction with the slightly acidic water as follows:

$$H_2O_2 + 2\,I^- + 2\,H^+ \longrightarrow 2\,H_2O + I_2 + I^- \longrightarrow I_3^-$$

This theory was supported by tests in solutions of varying acicity. Further equilibrium experiments were performed attempting to identify the intermediate complex, but the results were inconclusive.

There were four basic conclusions drawn from this work: (1) The reaction is of the second order, the rate being directly proportional to the concentrations of H_2O_2 and I^- and equal to 1.43×10^{-4} liters²/mole/second at 25° C. (2) The rate constant varies with temperature as, $d \log k/d\,T = 3704$. (3) The activation energy for the reaction equals 17 kcal/mole. (4) The most probable intermediate complex is IO^-.

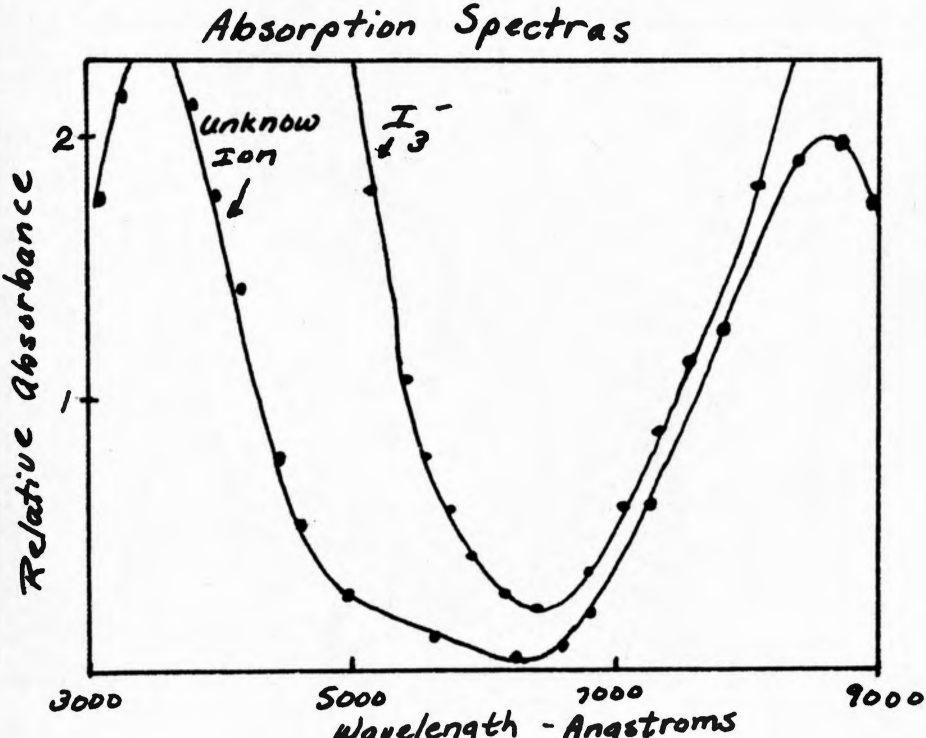

Figure 2

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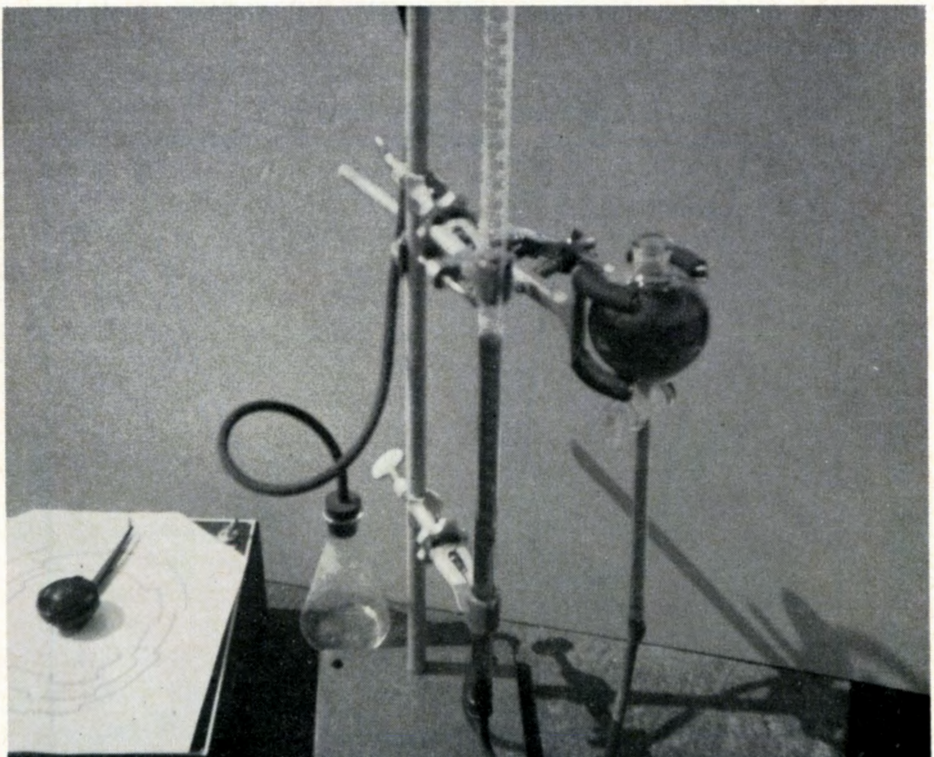

This exhibit, entitled "Chemical Kinetics of KI Catalyzed Hydrogen Peroxide Decomposition," won first place in the senior division, physical sciences, at the Quad-Cities Science Fair.