The Hong Kong Polytechnic University

Bsc(Hons) in Chemical Technology

Chemistry Laboratory III
Laboratory Report

Inorganic Chemistry Experiment 6

Title: **Analyzing First Order Kinetics – cis-trans isomerization of mercury dithizonate**

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Aim:

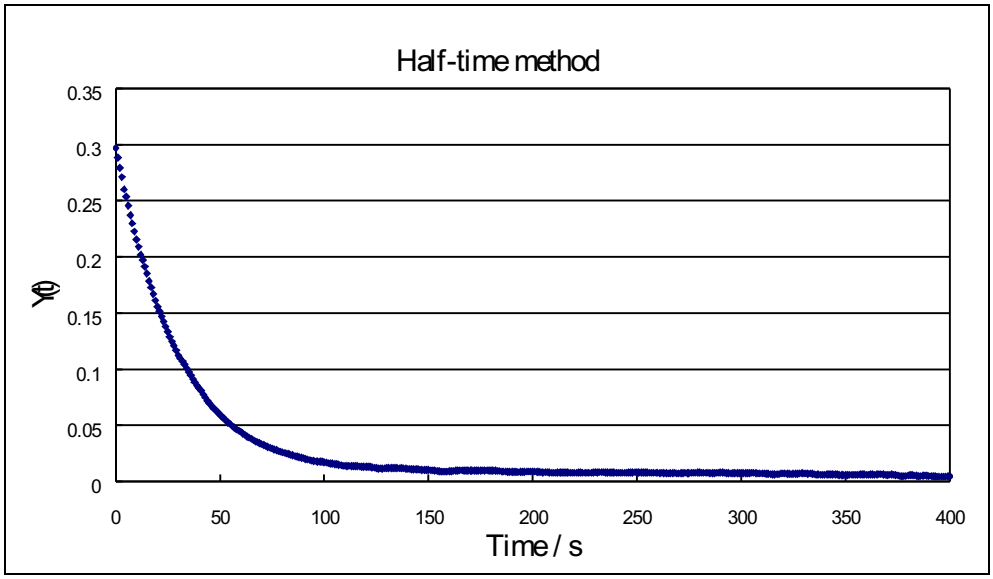
The purpose of this experiment is to analyze first-order kinetics and rate constant by using four general methods:

1. Half-time method
2. Semi-log method
3. Guggenhein's method
4. R/R_{Δ} method (ratios of rates).

Results and Data Treatment:

Half-time Method

From the data obtained (Appendix 1), a graph of absorbance Y(t) against time is plotted.



Graph 1

For 1st order kinetics,

$$\frac{(y_t - y_\infty)}{(y_0 - y_\infty)} = \frac{1}{2} \qquad (1)$$

$$t = t_{1/2} \qquad (2)$$

$$y_{t1/2} = (y_0 + y_\infty) / 2$$

From the data,

$y_0 = 0.2969208$

$y_\infty = 0$

$y_{t1/2} = (0.2969208 + 0) / 2$

$= 0.1484604$

From Graph 1,

At absorbance 0.1484604, $t_{1/2} = 21.5s$

By $\mathbf{k_{obs} = \ln 2 / t_{1/2}}$,

$k_{obs} = \ln 2 / 21.5$

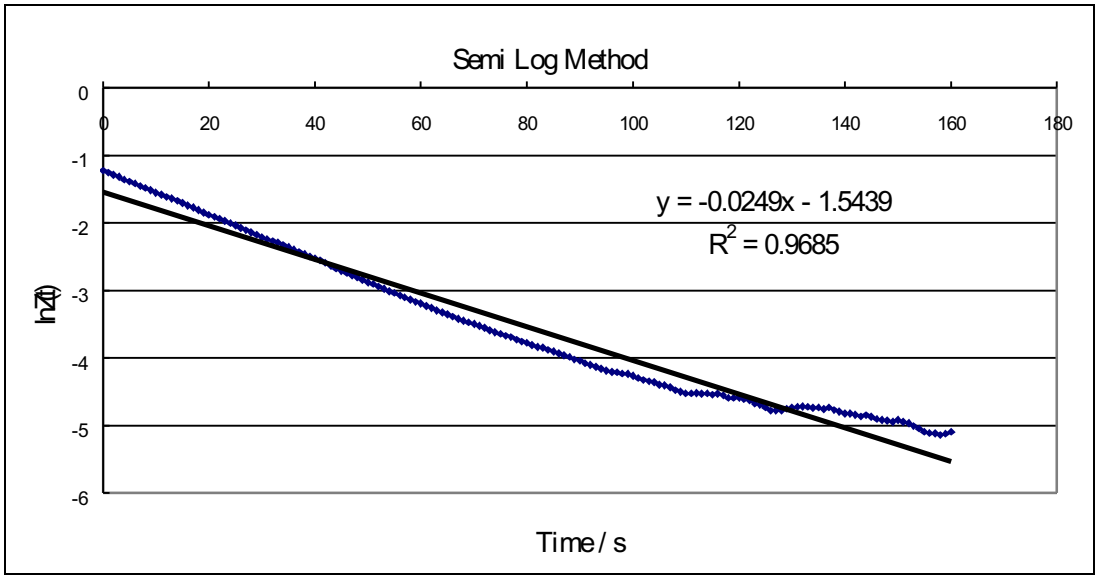
$= \mathbf{0.0322\ s^{-1}}$

Semi-log Method

$$\ln|y_t - y_\infty| = -k_{ds}\, t + \ln|y_0 - y_\infty|$$

A graph of $Z(t) = \ln[y_t - y_\infty]$ against time is plotted.

(The value of $\ln[y_t - y_\infty]$ refer to Appendix 3)



Graph 2

From the equation, y= -0.0249x – 1.5439

Slope of graph = $-k_{obs} = -0.0249$

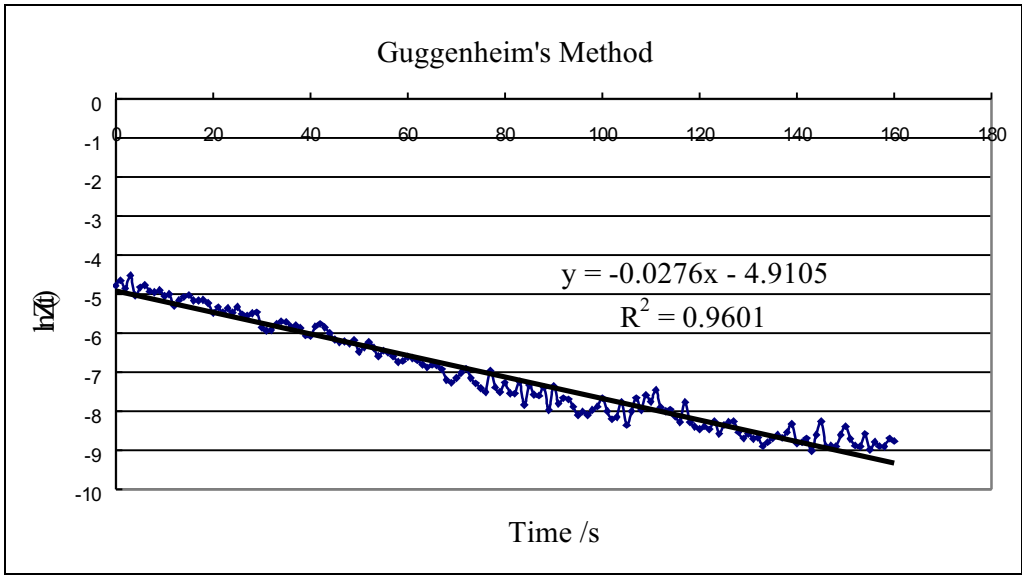
$\therefore\ k_{obs} = \mathbf{0.0249\ s^{-1}}$

Guggenhein's Method

$$\ln\left|y_{t+\Delta t} - y_t\right| = -k_{obs}\, t + (\exp(-k_{obs}\,\Delta) - 1)\ln\left|y_0 - y_\infty\right|$$

Take $\Delta t = 1$

A graph of Z(t) = ln[y(t+Δt)-yt] against time is plotted.
(The value of ln[y(t+Δt)-yt] refer to Appendix 3)



Graph 3

From the equation, y= -0.0276x – 4.9105
Slope of graph = $-k_{obs}$ = -0.0276

∴ k_{obs} = **0.0276 s^{-1}**

R/R△ Method (Ratios of Rates)

$$k_{obs} = \frac{\ln\left(R_t / R_{t+\Delta}\right)}{\Delta}$$

With pure first-order decays, the successive ratio must remain constant

$$k_{obs} = \frac{(\ln r_m)}{\Delta}$$

Where r_m is the mean value of the successive ratios $R_t/R_{t+\Delta}$ along the whole kinetic curve.

R = dy/dt

As Δ = 20

Table below is R in Successive 20 s interval

Rate	Time / s	Absorbance (y)	dy/dt	R_t / $R_{t+\Delta}$
0	0	0.2969208	-0.0084229	2.021965096
20	20	0.1556702	-0.0041657	1.784331363
40	40	0.08308411	-0.0023346	1.719107825
60	60	0.04393005	-0.00135803	1.869568315
80	80	0.02578735	-0.0007019	1.483869604
100	100	0.01699829	-0.00047302	1.785741035
120	120	0.0131073	-0.00021362	1.399960679
140	140	0.01098633	-0.00015259	1.25002048
160	160	0.008926392	-0.000137329	--------

Average of the R_t / $R_{t+\Delta}$ ($\mathbf{r_m}$) = **1.66432055**

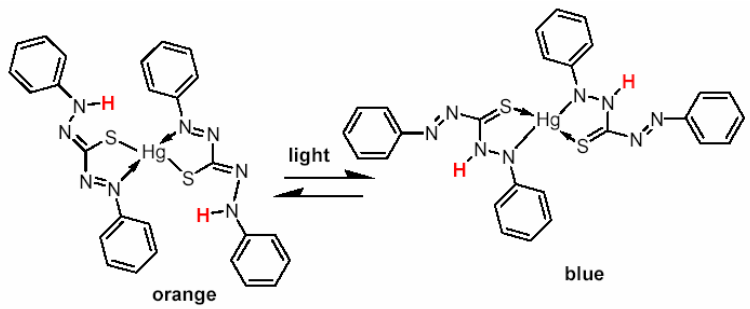
$$k_{ds} = \frac{(\ln\ r_m)}{\Delta}$$

k_{obs} = **0.025s^{-1}**

Discussions:

Mercury dithizonates were used in this experiment. Metal dithizonates have several interesting properties including photoactivation by light of wavelength greater than 350nm, reversible colour changes, photochemical forward and fast thermal return reactions, and log term stability to visible and near ultraviolet light.

The colour change accompanies the photoactivation of a cis-trans isomerization within the ligand as shown below.



The orange form of mercury dithizoate is photosensitive because it is ligand-centred with metal-ligand charge transfer character. The photochemical transition proceeds through a rotational movement of the dithizone in its complex with mercury.
In this experiment, dry xylene was used as solvent because the complex is soluble and stable in dry xylene. It can slow down the thermal return rate of the dark reaction.

The half-life was 21.5s. It is much shorter than typical half-time 120s. It is due to the cleanliness of glassware. Dust, water and other surface catalysis may speed up the reaction and shorter the half-life.

4 methods were used in this experiment. Only R/R_{Δ} method does not require linear regression and $Y\infty$. It is a combination of a differential and a time interval method and has several advantages.

1. It can be applied directly to the spectrophotometer tracings using simple graphical techniques.
2. With a slightly noisy recording, a small portion of the overall curve can be used. Results can thus be obtained quickly.
3. The validity of the pseudo-first-order approximation can be tested. It is valid if the R/R_{Δ} values remain constant.

Conclusion:

The rate constants (k_{obs}) determined by the four methods were

(a) Half-time Method = **0.0322 s^{-1}**

(b) Semi-log Method = **0.0249 s^{-1}**

(c) Guggenheim's Method = **0.0276 s^{-1}**

(d) R/R_{Δ} Method (ratio of rates) = **0.025s^{-1}**

All rate constants (k_{obs}) determined were in the usual range $5x10^{-3} < k_{obs} < 5 \times 10^{-2}$ s^{-1}

Reference:

1. R. L. Petersen, G. L. Harris, *J. Chem. Educ.* 1985, 62, 802.
2. A. T. Hutton, *J. Chem. Educ*. 1986, 63, 888.
3. B.Borderie, D. Lavabre, G. Levy, J. C. Micheau, *J. Chem. Educ.* 1990, 67, 459.