

Electronic Supplementary Information

Kinetics based on the base-catalyzed mechanism of click reaction between glycol dimercaptoacetate and glycidyl phenyl ether

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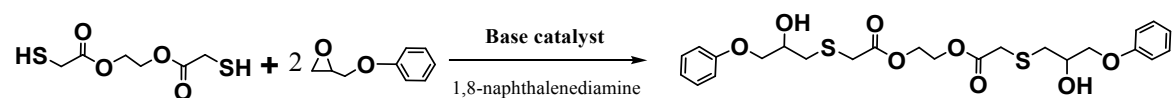
1. Experimental details

1.1 Materials

Glycol dimercaptoacetate and 1,8-naphthalenediamine were purchased from J&K Scientific. Glycidyl phenyl ether was purchased from Tokyo Chemical Industry Co., Ltd.. Acetone, hydrochloric acid, sodium hydroxide, potassium hydrogen phthalate were provided by Sinopharm Chemical Reagent. All materials were received and used without further purification.

1.2 Kinetics experiments

The kinetics experiments of thiol-epoxy reaction in bulk condition were carried out in a 100ml three-neck round-bottom flask with magnetic stirring under nitrogen atmosphere. The given proportion of glycol dimercaptoacetate and glycidyl phenyl ether were mixed in the above flask and heated to the specified temperatures. Then, base catalyst 1,8-naphthalenediamine was added to the flask and the timer was started. Samples were taken every twenty minutes through the reaction process. A real reaction scheme was shown as:



1.3 Analysis of epoxy concentration of samples

Samples were weighed precisely firstly before being added by excess hydrochloric acid in acetone solution. After a period time of standing in dark (enough time for reaction between hydrochloric acid and epoxy functional group), the samples were added by excess deionized water. Excess hydrochloric acid was ionized in water and the solution had electrical conductivity which is related to the concentration of excess hydrogen ion. The samples were analyzed by titration, using standard sodium hydroxide solution. The changes of conductivity of sample solutions were recorded by conductivity meter and the conductivity curve was drawn to determine the end point of titration. The blank experiment was needed to calculate the concentration of epoxy functional group of samples. The concentration of standard sodium hydroxide solution was standardized by dried potassium hydrogen phthalate before use.

1.4 Reaction conditions

The reaction conditions are listed in Table S1. The mass concentrations of base catalyst of all kinetic experiments are all kept constant except Run 9 and Run 10.

Table S1 Reaction conditions of the kinetics experiments of this thiol-epoxy reaction

Run	Molar Ratio of Thiol and Epoxy Functional Group	Catalyst Loading ^a	Temperature / °C
1	1:1	1 mol%	60
2	1:1	1 mol%	70
3	1:1	1 mol%	80
4	1:1	1 mol%	90
5	1:1	1 mol%	100
6	1:1	1 mol%	110
7	1:1	1 mol%	120
8	1:1	1 mol%	130
9	1:1	2 mol%	110
10	1:1	5 mol%	110
11	1.5:1	1.22 mol%	100

a: Catalyst loading is the molar ratio between base catalyst and epoxy functional group.

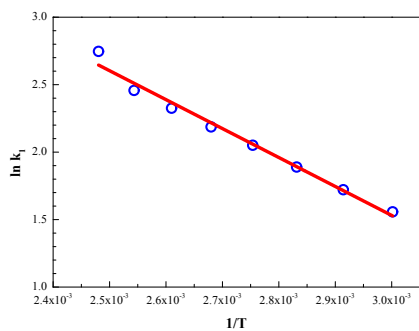
2. Kinetics model

The differential equations of consumption or generation rates of the seven kinds of substances in the mechanism were written as Eq.S1-7. The two thiol groups in glycol di(mercaptoacetate) are assumed to have the same activity.

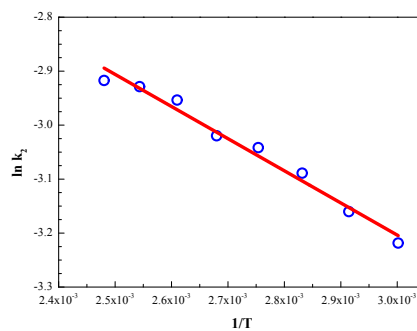
$$\left[\begin{array}{l} -\frac{dc_A}{dt} = k_1c_Ac_B + k_4c_Ac_F - k_2c_Cc_D \quad \text{Eq.S1} \\ -\frac{dc_B}{dt} = k_1c_Ac_B - k_2c_Cc_D - k_5c_Dc_F \quad \text{Eq.S2} \\ \frac{dc_C}{dt} = k_1c_Ac_B + k_4c_Ac_F - k_2c_Cc_D - k_3c_Cc_E \quad \text{Eq.S3} \\ \frac{dc_D}{dt} = k_1c_Ac_B - k_2c_Cc_D - k_5c_Dc_F \quad \text{Eq.S4} \\ -\frac{dc_E}{dt} = k_3c_Cc_E \quad \text{Eq.S5} \\ -\frac{dc_F}{dt} = k_4c_Ac_F + k_5c_Dc_F - k_3c_Cc_E \quad \text{Eq.S6} \\ \frac{dc_G}{dt} = k_4c_Ac_F + k_5c_Dc_F \quad \text{Eq.S7} \end{array} \right.$$

3. lnk - 1/T curves of each rate constant of elementary reactions

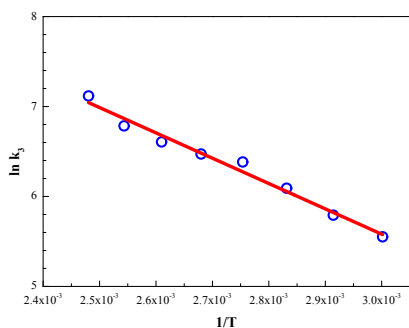
The $\ln k - 1/T$ curves of each rate constant are illustrated in Figure S1. All of these curves show fine linearity.



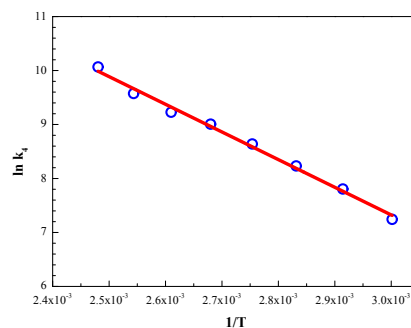
(a) $\ln k_1 - 1/T$ ($R^2=0.9821$)



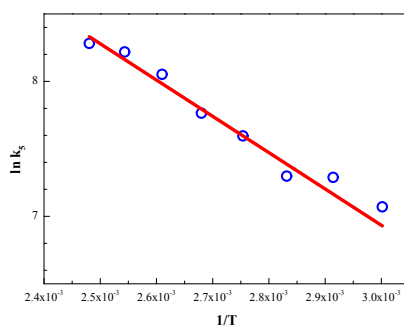
(b) $\ln k_2 - 1/T$ ($R^2=0.9778$)



(c) $\ln k_3 - 1/T$ ($R^2=0.9778$)



(d) $\ln k_4 - 1/T$ ($R^2=0.9930$)



(e) $\ln k_5 - 1/T$ ($R^2=0.9442$)

Figure S1 $\ln k - 1/T$ curves of each rate constant of elementary reactions

4. Concentration - reaction time curve of the alkoxide anion

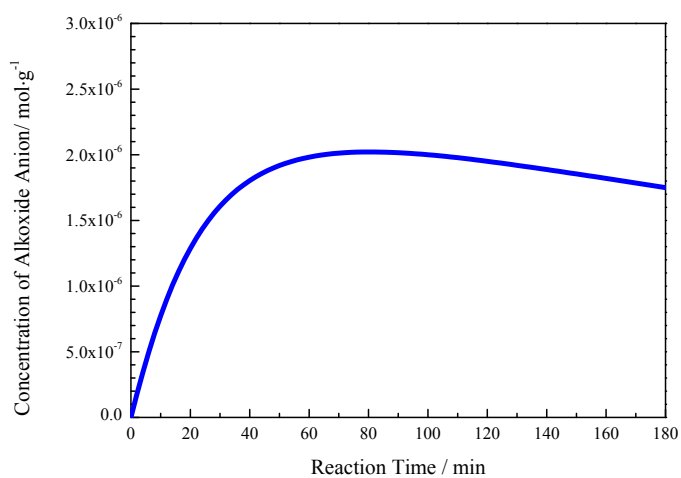


Figure S2 Concentration - reaction time curve of the alkoxide anion (Run 5)