# RESEARCH ON THE KINETICS OF THERMAL ISOMERIZATION REACTION OF MESOISOMER OF DIETHYL 2,3-DICYANO-2,3-DIPHENYLSUCCINATE IN AROMATIC COMPOUND SOLVENTS BY HPLC

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## ABSTRACT

The kinetics behaviour, activation parameters of thermal isomerization of meoisomer of diethyl 2,3-dicyano-2,3-diphenylsuccinate (1) in the aromatic compound solvents are investigated by external standard methods with HPLC at different temperatures of 90°C, 100°C, 110°C and 120°C, under protection of nitrogen gas. The relative error and the standard deviation of the quantitative analysis are less than $\pm 0.65\%$ and 0.35, respectively. The experimental results show that both equilibrium constant K and standard free energy $\Delta G^0$ of thermal isomerization reaction of compound 1 in different solvents are insensitive to the reaction temperature and the kinds of solvents.

The observed activation energy $E_a$ is nearly equal to the activation enthalpy $\Delta H$. However, the value of activation entropy $\Delta S$ is different and negative. In addition, the observed rate constant $k_{obs}$ is also insensitive to the kinds of solvents, but is greatly affected by the temperature.

## INTRODUCTION

The meoisomer of diethyl 2,3-dicyano-2,3-diphenylsuccinate (1) is a kind of excellent new-type initiator of vintyl-monomer polymerization. Under normal-temperature, it is quite stable.[1] Therefore, it is of great significance to research into the kinetics of thermalisomerization reaction of the compound 1 not only in theory but also in practice.

Peterson[2] had studied the dynamics of thermal decomposition of 2,3-dimethyl-2,3-diphenylsuccinonitrile in o-dichlorobenzene. De Jongh et al.[3] had studied the thermal decomposition process of dimethyl 2,3-dicyano-2,3-diphenylsuccinate with the help of NMR. In this paper, in order to investigate the thermal decomposition behaviour of compound 1, to explore how the aromatic compound solvents affect the reaction equilibrium constant K and the observed rate constant $k_{obs}$, the kinetics of thermal isomerization reaction of the meso-isomer 1 in chlorobenzene, methylbenzoate, phenylcyanide, ethylbenzene, and phenetole solvents are studied by HPLC, at different temperatures of 90°C, 100°C, 110°C, and 120°C under the protection of nitrogen gas.

## EXPERIMENTAL

### Chromatographic Apparatus

The chromatographic experiments were performed with a Model Hitachi 635AR HPLC equipped with a Hitachi 200-10 double beam spectrophotometer.

### Reaction Device

One of the three mouthes of pear-shaped bottle of 25mL is sealed with emulsion tube in order to draw out the sample by microinjector from the bottle; the other mouthes are equipped with a thermometer whose accuracy is 0.1°C and a spherical condensation tube sealed with nitrogen gas, respectively. The

pear-shaped bottle containing the test solution of compound **1** is dipped into the constant temperature oil bath which is controlled by the relay and the conductometer at the demanded temperature. The variation of reaction temperature is ±0.2°C.

## Chromatographic Condition

An analytical column (YWG-80-50 μm, 200 × 4.0mm i.d.) is used. Mobile phase is dioxane/n-hexane (10:90 v/v); flow rate is 1.5mL/min; working pressure is 8 MPa; wavelength of detection λ is 254nm; slit is 0.5nm.

## Reagents And Standard Samples

The chemical reagents of dioxane, n-hexane, chlorobenzene, methylbenzoate, phenylcyanide, ethylbenzene, and phentole are all analytical grade, and must be re-evaporated and filtered before using. The standard samples of the meso-isomer **1** and the di-isomer (**2**) of diethyl 2,3-dicyano-2,3-diphenyl succinate are obtained from the Department of Chemistry of Lanzhou University and their purity can satisfy the work needs after being identified by chromatograph.

## RESULTS AND DISCUSSION

## Qualitative Analysis

The reaction mechanism of thermal isomerization of compound **1** has been expounded in document[4] as follows:



(1)          (R)          (2)
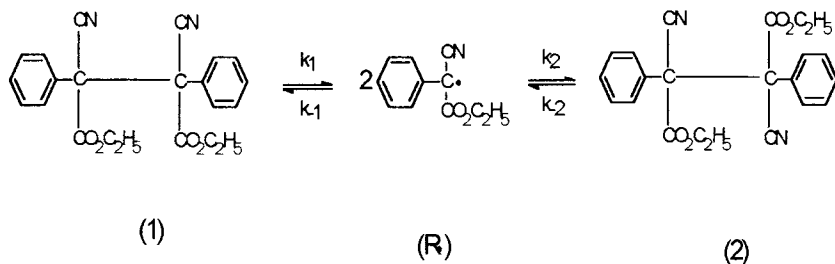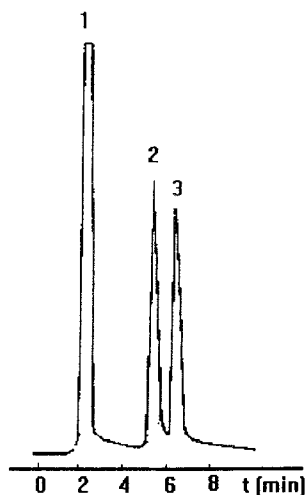
**Figure 1.** Chromatogram of the mixed solution. 1-ethylbenzene; 2-compound **1**;
3-compound **2**.

A dynamic equation of typical first-order opposing reaction is obtained.

$$\ln \left[ \chi_e/(\chi_e - \chi) \right] = (k + k') \cdot t = k_{obs} \cdot t \tag{1}$$

Here. $k = k_1 k_2/(k_{-1} + k_2)$. $k' = k_{-1}k_{-2}/(k_{-1} + k_2)$; the compound **1** is the
reactant; the compound **2** is the product; $(\chi_a)$ is the original concentration;
When the reaction is at any time and reaches the equilibrium state, the
concentrations of compound **2** are $\chi$ and $\chi_e$, respectively.

The relative equilibrium constant K is the following:

$$K = k/k' = \chi_e/(\chi_a - \chi_e) \tag{2}$$

The pear-shaped bottle, containing the solution of sample prepared in
ethylbenzene on the concentration of 0.219mol/L for the compound **1**, is dipped
into the constant temperature oil bath, then is heated for one hour under the
protection of $N_2$ at 100°C constant temperature. The reaction mixed solution is
analysed with the Model Hitachi 635AR HPLC. The acquired chromatogram
of separation is shown in Figure 1.

## Table 1

### Observed Rate Constants of Thermal Isomerization of Compound 1

$k_{obs} \times 10^4$

| Solvent | 90°C | 100°C | 110°C | 120°C |
|---------|------|-------|-------|-------|
| Chlorobenzene | 0.91 | 2.87 | 7.71 | 12.98 |
| Methylbenzoate | 0.87 | 2.77 | 6.62 | 12.07 |
| Phenylcyanide | 0.77 | 2.68 | 5.82 | 11.42 |
| Ethylbenzene | 0.72 | 2.47 | 5.54 | 10.08 |
| Phenetole | 0.69 | 2.33 | 5.37 | 9.93 |

Using the qualitative method of classical retention value, it is found that the retention times of three peaks in Figure 1 are identical with the ethylbenzene, the standard samples of 1 and 2, respectively. On a Model Hitachi 635AR HPLC, the qualitative method of UV spectrum of stop flowing scanning[5] is used to obtain the UV spectra of the three peaks in Figure 1, which also correspond respectively with the UV spectra of the ethylbenzene and the standard samples. This confirms the results in Figure1, where the three peaks are ethylbenzene, 1 and 2, respectively.

It has been shown that under the chosen experimental condition,only thermal isomerization of compound 1 occurs without having any other side reactions.

## The Dynamic Parameters of the Thermal Isomerization Reaction of Compound 1

The solutions of samples are prepared in chlorobezene, methylbenzoate, phenylcyanide, ethylbenzene, and phenetole solvents, respectively on the original concentrations of 0.219mol/L for the compound 1, and are heated under the protection of $N_2$ at different temperature of 90°C,100°C,110°C, and 120 °C. At regular intervals, the reacted mixed solution was taken out with 5 μL microinjector and injected immediately into the Model Hitachi 635AR HPLC for analysing and determining the contents of 1 and 2 with the external standard method until the reaction reaches the equilibrium state. The concentrations of 1 and 2 are ($\chi_a$ - $\chi_e$) and $\chi_e$, respectively.

## Table 2

### Activation Parameters of Thermalisomerization of Compound 1

| Solvent | $E_a$ | Temperature | 90°C | 100°C | 110°C | 120°C |
|---------|-------|-------------|------|-------|-------|-------|
| | | $\Delta H$ | 24.78 | 24.76 | 24.74 | 24.72 |
| Chlorobenzene | 25.53 | $\Delta S$ | -8.83 | -8.88 | -8.94 | -8.99 |
| | | $\Delta G^0$ | -1.61 | -1.65 | -1.70 | -1.74 |
| | | $\Delta H$ | 24.18 | 14.16 | 24.14 | 24.12 |
| Methylbenzoate | 24.94 | $\Delta S$ | -10.58 | -10.63 | -10.69 | -10.74 |
| | | $\Delta G^0$ | -1.61 | -1.65 | -1.70 | -1.74 |
| | | $\Delta H$ | 24.58 | 24.56 | 24.54 | 24.52 |
| Phenylcyanide | 25.29 | $\Delta S$ | -9.78 | -9.84 | -9.89 | -9.94 |
| | | $\Delta G^0$ | -1.61 | -1.65 | -1.70 | -1.74 |
| | | $\Delta H$ | 24.18 | 24.16 | 24.14 | 24.12 |
| Ethylbenzene | 24.92 | $\Delta S$ | -10.96 | -11.01 | -11.06 | -11.11 |
| | | $\Delta G^0$ | -1.61 | -1.65 | -1.70 | -1.74 |
| | | $\Delta H$ | 24.38 | 24.36 | 24.34 | 24.32 |
| Phenetole | 25.12 | $\Delta S$ | -10.48 | -10.53 | -10.59 | -10.64 |
| | | $\Delta G^0$ | -1.61 | -1.65 | -1.70 | -1.74 |

\* Unit of $\Delta H$ is kcal/mol; Unit of $\Delta S$ is cal/mol.k; unit of $\Delta G^0$ is kcal/mol; Unit of $E_a$ is kcal/mol

Then the reaction equilibrium constant K is calculated with the equation (2). The experimental results show that the value of K is $9.28 \pm 0.05$ and does not vary with temperature. The result is correspondent with Peterson's reported.[2] The data are determined to the thermal isomerization reaction of compound 1 in these five aromatic compound solvents and at different temperatures, respectively. According to equation (1), taking $\ln[\chi_e/(\chi_e - \chi)]$ as coordinate Y, regarding the reaction time as coordinate X, the observed rate constant $k_{obs}$ is calculated by the least square method as shown in Table 1. The data are treated with the linear regression, the correlative coefficients r are 0.9994-0.9999, the lines are well linear relation and pass nearly the zero of coordinate.

According to Arrhenius equation, taking $lnk_{obs}$ as coordinate Y, regarding the reciprocal of the reaction absolute temperature (1/T) as coordinate X, the data are treated with the linear regression, the correlative coefficients r are 0.9992-0.9999, and obtained the lines of good linear relation, which are parallel. Then the relative activation parameters are calculated with the least square method, the results are given in Table 2.

To sum up, the reaction equilibrium constant K and the standard free energy $\Delta G^0$ of thermalisomerization reaction of compound 1 in these five aromatic compound solvents are insensitive to the reaction temperature and the kinds of solvents. The observed rate constant $k_{obs}$ is also insensitive to the kinds of solvents, but is greatly affected by the temperature. The observed activation energy Ea is nearly the equal to the activation enthalpy $\Delta H$. However, the value of activation entropy $\Delta S$ is different and negative. As compared with Jongh's reported resultant[3] is almost identical.

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