Determination of kinetic transformation of two geometrical isomers of the $\text{Fe}^2+$ PDT$_3^2+$ by high performance liquid chromatography

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Abstract: The kinetic transformation of the two isomers of the $\text{Fe}^2+$ PDT$_3^2+$ PDT$_3^2+$ 2-pyridyl-5-b-diphenyl-1-p-triazine was studied by high performance liquid chromatography. The transformation between two isomers was proved to be treated kinetically as the first-order reaction. At different reaction temperatures the linear regression equations between $x, \ln \frac{x}{1-x}$ and $t$ were as follows: $x, \ln \frac{x}{1-x} = 0.082t + 0.729$, $r^2 = 0.9911$, $T = 45 \, ^\circ \text{C}$; $x, \ln \frac{x}{1-x} = 0.049t + 0.598$, $r^2 = 0.9987$, $T = 35 \, ^\circ \text{C}$, where $x$ is the conversion of the isomer, $t$ is the reaction time, $r^2$ is the correlation coefficient. The activation enthalpy $\Delta H^\ddagger$, activation entropy $\Delta S^\ddagger$, and activation energy $\Delta E_a$ characterizing the kinetic transformation were as follows: $\Delta H^\ddagger = 103.84 \, \text{kJ mol}^{-1}$, $\Delta S^\ddagger = 271.93 \, \text{J mol}^{-1}$, $\Delta E_a = 86.47 \, \text{kJ mol}^{-1}$. $K^{-1} \Delta E_a = 94.43 \, \text{kJ mol}^{-1}$. $K^{-1} \Delta E_a$ is the dynamic isomer-fac-isomer. $K^{-1} \Delta E_a$ is the dynamic isomer-mer-isomer-fac-isomer.

Key words: high performance liquid chromatography, HPLC, Fe$_3^2+$ PDB$_3^2+$ 2-pyridyl-5-b-diphenyl-1-p-triazine, $\text{Fe}^2+$ metal complex, geometrical isomers, kinetic transformation.
1. PDT Fe PDT₃²⁺ Fe

PDT

Schilt

Fe PDT₃²⁺ Fe

Fe PDT₃²⁺ Fe

Fe PDT₃²⁺ Fe

PDT

2. 2.1

HP1100 Agilent Agilent Agilent

G1365B Agilent Agilent

G2170AA Tedia Tedia

PDT Sigma-Aldrich Sigma-Aldrich

2.2

Shim-pack ODS C8 Eclipse XDB-C8 4.6 mm × 150 mm μm Agilent Agilent

70:30 20 mmol/L 20 mmol/L pH 4.65 555 nm 20 μL

2.3

0.039 2 g Fe NH₄SO₄ 0.1 H₂O pH 2 100 mL 100 mL 4 mL 1 mmol/L PDT 100 mL 100 mL

F₆PDT₂⁻ Fe

HPLC

3. 3.1

1 kₐ kₐ kₐ kₐ kₐ kₐ

3.1 x₀ t 1

dx/dt = kₐ (1 - x) - kₐ x

x₀ ln (x₀ - x) = kₐ (t - t₀)

K_v = kₐ / kₐ = x_v / (1 - x_v)

Eₐ = RT \int ln k dT

ΔEₐ = R \left( \frac{T_2}{T_2 - T_1} \right) ln \frac{k_2}{k_1}

ln k = -ΔH/RT + ΔS/R
3.2 Palmer \[14]\]

High-performance liquid chromatography (HPLC) for measuring the dynamic transformation between isomers

In reversed-phase chromatography, the elution order of enantiomers is opposite to that of adsorption chromatography, i.e., the face isomer will be eluted first.

It is believed that the elution order of isomers on the chromatogram mainly depends on their dipole interactions; the dipole interactions of the face isomer are stronger than those of the axial isomer, and the stronger the dipole interaction, the greater the molecular polarity and the greater the interaction force with other molecules. In reversed-phase chromatography, the polarity of the stationary phase is less than that of the mobile phase, so the dipole interaction of the face isomer with the mobile phase is greater, and thus the face isomer is eluted preferentially.

From the chromatogram, it can be seen that with the increase in reaction time, the face isomer gradually transforms into the axial isomer, so its peak height and peak area gradually decrease, while the peak height and peak area of the axial isomer correspondingly increase. When the reaction proceeds for approximately 40 min, the peak areas of the two isomers remain almost constant, indicating that the transformation between isomers is in equilibrium (see Fig. 2). The experiment also shows that after reaching equilibrium, the sum of the peak heights and areas of the two isomers is constant, only depending on the concentration of the complex.

Figure 1 shows the chromatograms of two geometrical isomers at different times under a constant temperature of 45 °C.

1. a. 0 min b. 4 min c. 9 min d. 14 min e. 41 min f. 780 min
   1. face-isomer 2. mer-isomer.

3.3 Fe PDT⁻²⁺  metal complex

The dynamic transformation of the two geometrical isomers at different temperatures can be observed from Fig. 3, which shows the linear regression equations during the kinetically transformation of the two geometrical isomers at different temperatures.
速率常数

（力学相互转变过程中的活化焓（构体转变））。

- \[\Delta H^i = 103.84 \text{ kJ} \cdot \text{mol}^{-1}\]

\[\Delta S^i = 271.93 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\]

\[\Delta E_a = 86.74 \text{ kJ} \cdot \text{mol}^{-1}\]

\[\Delta H^i = 106.47 \text{ kJ} \cdot \text{mol}^{-1} \cdot \Delta S^i = 257.65 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\]

\[\Delta E_a = 94.43 \text{ kJ} \cdot \text{mol}^{-1}\]

<table>
<thead>
<tr>
<th>表1</th>
<th>热力学常数和动力学参数</th>
<th>取样温度</th>
<th>(k_c)</th>
<th>(k_i)</th>
<th>(k_{i/s}^{-1})</th>
<th>(k_i/s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>94.05</td>
<td>15.81</td>
<td>2.07 \times 10^{-2}</td>
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<tr>
<td>35</td>
<td>93.89</td>
<td>15.37</td>
<td>3.60 \times 10^{-2}</td>
<td>0.23 \times 10^{-2}</td>
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<tr>
<td>40</td>
<td>94.02</td>
<td>15.72</td>
<td>8.10 \times 10^{-2}</td>
<td>0.52 \times 10^{-2}</td>
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<tr>
<td>45</td>
<td>93.69</td>
<td>14.85</td>
<td>13.68 \times 10^{-2}</td>
<td>0.92 \times 10^{-2}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[\ln k = -12490/T + 32.708\]

\[r^2 = 0.993\]

\[y = -12806x + 30.99\]

\[r^2 = 0.996\]

**图4** 线性回归方程在温度-1/T条件下和反应速率常数k期间间的线性关系。