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The Dynamic NMR of Isomerization of Unsymmetrical Dialkylthiolatohexacarbonyldiiron

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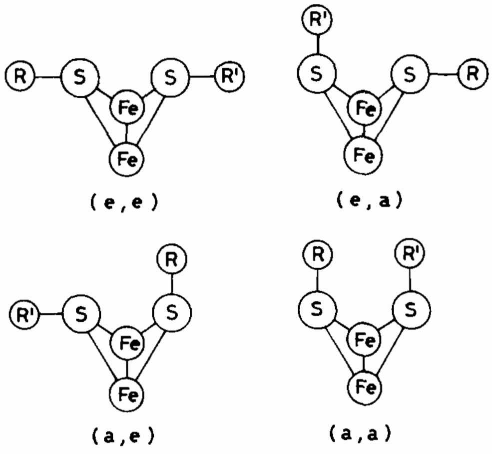
Abstract

The kinetics of isomerization reaction of unsymmetrical dialkylthiolatohexacarbonyldiiron (μ-ph-CH_2S)(μ'-tBuS)$Fe_2(CO)_6$ has been studied by means of dynamic ^1H NMR within the temperature range 35 to 110 °C with 10 selected points. The changes of line width of the ^1H NMR spectrum at various temperatures were studied in a more convenient way, and the related kinetic parameters have been obtained.

Introduction

A series of compounds with the general formula (μ-RS)(μ'-R'S)$Fe_2(CO)_6$ should have four isomers in theory, as shown in Fig. 1 [1]. But in fact, only three were found, the isomer (a,a) was absent. It may be due to the fact that in the isomer (a,a) the distance between R and R′ is so short that the repulsive force between them is too great for a stable isomer (a, a) to exist.



(e,e) (e,a)

(a,e) (a,a)

Fig. 1. Isomers of the compounds.

It has been shown that the isomers of the compounds can mutually transform into each other [2, 3]. Some authors have studied the kinetics of isomerization of symmetrical compounds $(MeS)_2Fe_2(CO)_6$ [4] and (t-BuS)$_2Fe_2(CO)_6$ [5]. But the isomerization of such unsymmetrical compounds has not been reported in the literature.

It was found experimentally that the ^1H NMR spectrum of the compound (phCH_2S)(t-BuS)$Fe_2(CO)_6$ at room temperature was time independent (in fact, equilibrium was reached). In this paper we report on the kinetics of the isomerization reaction by means of temperature dependent ^1H NMR spectra.

Experimental

The compound (μ-phCH_2S)(μ'-tBuS)$Fe_2(CO)_6$ was synthesized and confirmed by elemental and IR analysis as reported earlier [6].

Equipment used: FX-90Q FT-NMR spectrometer (JEOL Company, Japan) with additional temperature set, selected temperature range 35–110 °C with accuracy ±1 °C, $CDCl_3$ solution, 5 mm sealed tubes filled with pure nitrogen or argon.

Figure 2 illustrates a ^1H NMR spectrum of solution of the compound at room temperature. According to Fig. 2, there are three isomers existing in solution, as shown in Fig. 3.

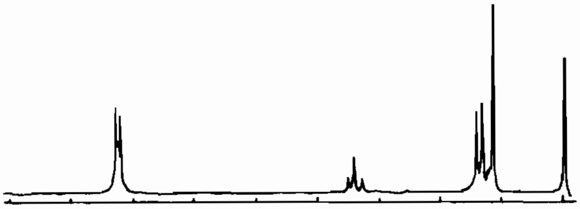


Fig. 2. ^1H NMR spectrum at room temperature.

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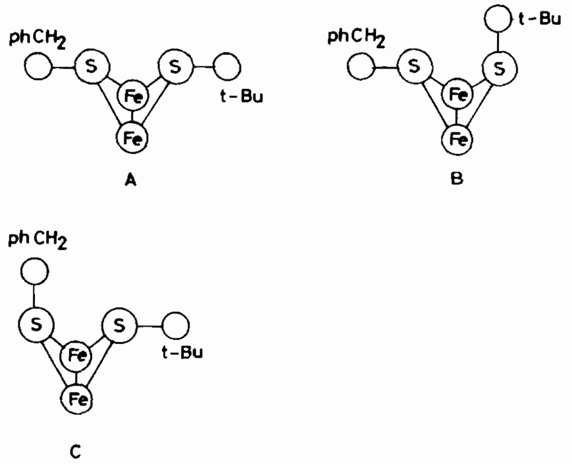

Fig. 3. Three isomers in solution.

As the temperature rises, the shape of the peaks of respective isomers obviously changes. The ^{1}H NMR spectra of the $-CH_2-$ part of the tolylene group at various temperatures are given in Fig. 4.

In Fig. 4 we find that as the temperature increases from 35 to 65 ℃, the line widths of the signals A and B increase, and consequently, the peaks A and B approach each other and coalesce at 65 ℃. But at the same time, there is no obvious change in the line width of peak C. From the above observation we may conclude that in the temperature range 35–65 ℃ a rapid transformation between isomer A and B is dominating, and the rate of transformation of isomer C to A/B is much slower. At temperatures above 75 ℃ the peaks A/B have coalesced, while peak C broadened and afterwards the rate of isomerization of isomer C became more rapid and finally coalesced with A/B at 110 ℃.

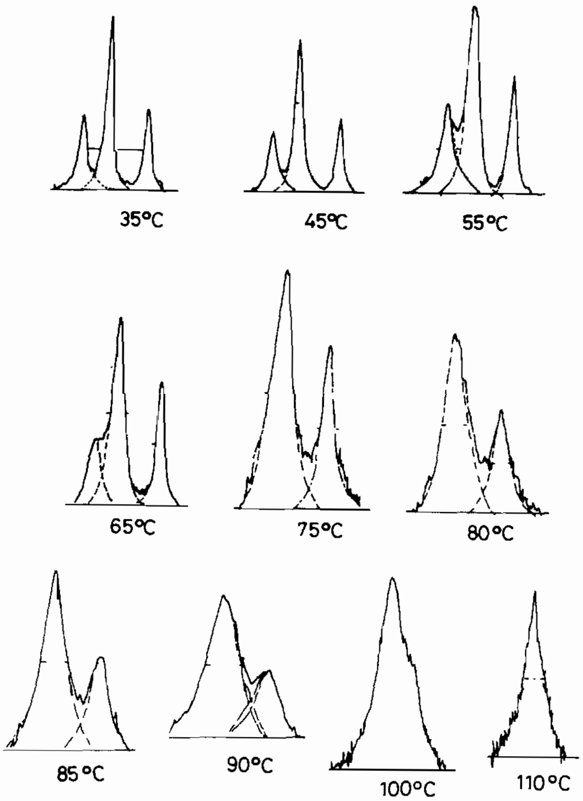

Fig. 4. ^{1}H NMR spectra at various temperatures.

Results and Discussion

The theoretical study of the dynamic system of fast exchange in N positions is based generally on the GMS theory [7, 8] or density matrix theory [9]. The line shape of the NMR spectrum is analysed by a computer aided program and the rate of exchange is calculated. But our particular system can be treated in a more convenient and efficient way. The results obtained were very satisfactory.

The formulas used are [10]:

$$\pi\Delta\nu_{1/2}(\mathrm{A}) = \frac{1}{T_2\mathrm{A}} + \frac{1}{\tau_\mathrm{A}} \qquad\qquad (1)$$
$$\pi\Delta\nu_{1/2}(\mathrm{B}) = \frac{1}{T_2\mathrm{B}} + \frac{1}{\tau_\mathrm{B}}$$

where $\Delta\nu_{1/2}$ is the line width; $1/\pi T_2$, the line width without exchange; τ_A and τ_B, the average lifetime in the position A and B; $1/\tau_A$ and $1/\tau_B$ are rate constants of A → B and B → A respectively.

After the coalescing, formula (2) is employed for the calculation [11]:

$$\pi\Delta\nu_{1/2} = \frac{N_\mathrm{A}}{T_2\mathrm{A}} + \frac{N_\mathrm{B}}{T_2\mathrm{B}} + N_\mathrm{A}{}^2 N_\mathrm{B}{}^2 \times (\mathring{w}_\mathrm{A} - \mathring{w}_\mathrm{B})(\tau_\mathrm{A} + \tau_\mathrm{B}) \qquad (2)$$

where N_A and N_B are the probability distribution of A and B respectively; $\mathring{w}_A - \mathring{w}_B$ equals 2π times the difference of frequences of A,B without exchange.

At temperatures below 65 ℃, formula (1) was used, and at temperature above 75 ℃ formula (2) was used with addition of a term $1/\tau_{AB}$ which has the following form:

$$\pi\Delta\nu_{1/2} = \frac{N_\mathrm{A}}{T_2\mathrm{A}} + \frac{N_\mathrm{B}}{T_2\mathrm{B}} + N_\mathrm{A}{}^2 N_\mathrm{B}{}^2 \times (\mathring{w}_\mathrm{A} - \mathring{w}_\mathrm{B})(\tau_\mathrm{A} + \tau_\mathrm{B}) + \frac{1}{\tau_\mathrm{AB}} \qquad (3)$$

Formula (3) was used for peaks A,B and formula (1) was used for peak C. Through these formulas we can obtain the rate constants of exchange of isomers A,B and C respectively.

TABLE I. Line Widths and Rate Constants at Various Temperatures

<table>
<tr><th>Temperature (°C)</th><th>$\Delta\nu_{1/2}(A)$ (Hz)</th><th>$\Delta\nu_{1/2}(B)$ (Hz)</th><th>$\Delta\nu_{1/2}(C)$ (Hz)</th><th>$\frac{1}{\tau_A}$ (s^{-1})</th><th>$\frac{1}{\tau_B}$ (s^{-1})</th><th>$\frac{1}{\tau_C}$ (s^{-1})</th><th>$\frac{1}{\tau_{AB}}$ (s^{-1})</th></tr>
<tr><td>35</td><td>2.22</td><td>2.39</td><td>2.78</td><td>1.63</td><td>1.87</td><td></td><td></td></tr>
<tr><td>45</td><td>3.07</td><td>2.52</td><td>2.24</td><td>4.30</td><td>2.28</td><td></td><td></td></tr>
<tr><td>55</td><td>4.12</td><td>3.73</td><td>2.65</td><td>7.59</td><td>6.08</td><td></td><td></td></tr>
<tr><td>65</td><td>4.46</td><td>4.43</td><td>2.55</td><td>8.68</td><td>8.26</td><td></td><td></td></tr>
<tr><td>75</td><td colspan="2">7.57</td><td>4.65</td><td>17.5</td><td>13.8</td><td>6.75</td><td>2.05</td></tr>
<tr><td>80</td><td colspan="2">8.02</td><td>5.61</td><td>22.3</td><td>17.4</td><td>9.77</td><td>3.39</td></tr>
<tr><td>85</td><td colspan="2">8.71</td><td>6.45</td><td>28.1</td><td>21.7</td><td>12.4</td><td>4.76</td></tr>
<tr><td>90</td><td colspan="2">10.41</td><td>7.89</td><td>35.3</td><td>27.1</td><td>16.9</td><td>7.00</td></tr>
<tr><td>100</td><td colspan="3">23.45</td><td></td><td></td><td></td><td></td></tr>
<tr><td>110</td><td colspan="3">25.57</td><td></td><td></td><td></td><td></td></tr>
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TABLE II. Parameters of Activation of Isomerization

k	$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta S^{\ddagger}$ (J/mol K)
k_{A-B}	46.2	−89.8
k_{B-A}	44.4	−96.8
k_{C-AB}	60.0	−57.8
k_{AB-C}	(81.7)	(−5.3)

TABLE III. Some Constants Without Isomerization.

Isomer	$\frac{1}{\pi T_2}$ (Hz)	N	$\nu°$ (Hz)	$w°$ (Hz)
A	1.7	0.23	313.5	1969.80
B	1.8	0.50	305.6	1920.14
C	2.5	0.27	293.7	1845.40

From the experiment, line widths of each peak and calculated rates $1/\tau$ of isomerization are listed in Table I, the kinetic parameters are listed in Table II, some used constants without exchange (from low temperature spectrum) are listed in Table III.

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