Activation Energy for Addition of Allyl Radical to Allene

Daisuke NOHARA* and Tomoya SAKAI

Dept. of Chemical Reaction Engineering, Faculty of Pharmaceutical Sciences,
Nagoya City University, Mizuho-ku, Nagoya 467

(Received March 13, 1991)

The Arrhenius parameters for addition of the allyl radical to allene were obtained. Experiments were conducted by use of an atmospheric flow apparatus at temperatures between 450 and 510°C. The allyl radical was prepared by pyrolyzing the vapor of diallyl oxalate. The activation energy and the A factor evaluated were 23 kJ mol⁻¹ and 10⁰.₆ cm³ mol⁻¹ s⁻¹, respectively. These values are comparable to those for addition of the ethyl or the propyl radical to ethylene. This result was contrary to the expectation that the activation energy to be obtained should be larger than that with the ethyl or the propyl radical by stabilization due to allyl-resonance. The energy levels of the allyl radical formed in the present experiment are discussed.

1. Introduction

The allyl radical is one of the radicals most extensively investigated in terms of its resonance or electron-delocalization energy. Such resonance or delocalization invests the radical with diene-like character, which probably contributes to the highly selective production of C₅ cyclic compounds in reactions with unsaturated hydrocarbons. This type of reaction is somewhat analogous to the Diels–Alder reaction of butadiene which produces C₅ cyclic compounds with olefins as illustrated below:

\[
\begin{align*}
\text{Allyl radical} + \text{Allene} & \rightarrow \text{Cyclic products} + \text{Acyclic products}
\end{align*}
\]

The reason that the concerted mechanism is excluded in the latter scheme is the fact that the concurrent production of acyclic products was observed in most cases.

How large is the activation energy for the elementary addition of the allyl radical possessing such character compared to that for the addition of methyl, ethyl, or propyl radical? The authors have studied the behavior of the allyl radical reacting with several unsaturated hydrocarbons, and they have intended (1) to clarify the product distribution in the individual cases and to make a comparative kinetic study on the formation of allyl-addition products, and (2) to evaluate the activation energy for the elementary addition of the allyl radical to unsaturated hydrocarbons. It was revealed that, conspicuously with acetylene, the addition of the allyl radical preferred producing cyclic products. However, not only the difficulty in quantitative measurement of the substrate hydrocarbon consumed by such addition but also the occurrence of side reactions of the substrate hydrocarbon itself, would retard the evaluation of the activation energy.

In the present experiments with allene employed as another substrate hydrocarbon, not only the elimination rate of allene but also the amounts of allene consumed by addition of the allyl radical were measurable with sufficient reliability to perform a kinetic analysis. Accordingly, the Arrhenius parameters for the elementary addition of the allyl radical to allene could be evaluated. In this paper, the method for obtaining these parameters and the results are reported. The details of allyl-addition products and their formation kinetics are reported in a separate paper.

2. Experimental

As in previous cases, diallyl oxalate (DAO) was used as precursor of the allyl radicals. The apparatus used was an ordinary atmospheric flow system, and the reactor was an annular quartz cylinder of 200 mm length and 10.6 mm i.d. equipped coaxially with a thermowell of 7.2 mm o.d. The reactor was positioned in an electrically heated stainless block of 180 mm length, 18 mm i.d. and 55 mm o.d. The tempera-
ture profile of the reactor was measured for each run, and the residence time was determined by the method of Hougen and Watson\textsuperscript{15}. Five levels of reaction temperature were designated between 430 and 510°C. Residence times thus obtained at designated temperatures were between 2 and 17 s.

Allene gas purchased contained ca. 0.2% of chloropropene as impurity, which was completely removed by adsorption on activated carbon. Allene thus purified was diluted with deoxygenated nitrogen to about 1.6% concentration. By use of a microfeeder, DAO was fed into the evaporator equipped at the reactor inlet to vaporize and then was introduced into the reactor with a flow of diluted allene gas. The vapor concentration of DAO was set around 2.5 vol% of the total inlet gas.

Reactants and products were analyzed by FID and TCD gas chromatographs and by a GC-MS.

3. Method of Kinetic Analysis

DAO employed as a source material of the allyl radical (allyl-) is almost uniquely pyrolyzed at the very initial stage of reaction along the following scheme\textsuperscript{16}:

\[
\text{DAO} \rightarrow 2\text{allyl}^- + 2\text{CO}_2
\]

Most of the allyl radicals formed produce biallyl through recombination:

\[
\text{2allyl}^- \xrightarrow{k_{\text{add}}} \text{biallyl}
\]

The recombination, whose rate constant, \(k_r\), was available\textsuperscript{3,4,17,18}, was adopted as the reference reaction in the present kinetic analysis. The remaining allyl radicals either produced propylene or added to allene to produce allyl-addition products as follows.

\[
\text{allyl}^- + \text{allene} \xrightarrow{k_{\text{add}}} \text{C}_6 \text{radical intermediates} \xrightarrow{\text{---}} \text{allyl-addition products}
\]

The rate constant, \(k_{\text{add}}\), represents one for the elementary addition of the allyl radical to allene. From the following relationship, \(k_{\text{add}}\) can be evaluated by measuring the rates of allene elimination and biallyl formation. This relationship is strictly valid where the total consumption of allene is attributed to the addition of the allyl radical, and the biallyl formation is only due to the recombination of allyl radicals.

\[
-d[\text{allene}] / dt = k_{\text{add}}[\text{allyl}^-][\text{allene}]
\]

4. Results and Discussion

The products in the thermal reaction between allene and DAO were a large amount of carbon dioxide, biallyl and propylene, ethylene, methyl-acetylene, butadiene, two methylenecyclopentene isomers, and 2-methyl-1,4-pentadiene. The last three compounds are considered as allyl-addition products. Additionally, there were produced minor products which were difficult to identify and which included nine species of C\(_5\)’s (including 1-pentene, cyclopentene and cyclopentadiene) and 13 species of C\(_6\)’s at maximum. Methane, ethane, and acetylene were also minor products. The amounts of products which are regarded as derived from allene were shown in Table 1. In the thermal reaction of allene itself, \textit{i.e.}, without addition of DAO, the major product was methyl-acetylene whose amount at each residence time was listed together in parentheses in Table 1. The C\(_5\) and C\(_6\) products were formed in trace amounts. The maximum conversion of allene in these blank experiments was about 0.5%. The thermal decomposition of DAO underwent stoichiometrically, as reported in the literature\textsuperscript{16}, to produce carbon dioxide and biallyl. Accordingly, the various species of C\(_5\)’s and C\(_6\)’s (Table 1) formed in small amounts should be produced obviously via the addition of the allyl radical to allene.

\[
-d[\text{allene}] / dt = k_{\text{add}}[\text{allyl}^-][\text{allene}]
\]

\[
k_{\text{add}} = k_{\text{add}}[\text{allyl}^-][\text{allene}]
\]

\[
d[\text{biallyl}] / dt = -k_1[\text{allyl}^-]^2
\]

### Table 1 Products Produced by Consumption of Allene and Allene Balance at 510°C

<table>
<thead>
<tr>
<th>Residence time [s]</th>
<th>DAO conversion [%]</th>
<th>Allene conversion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.15</td>
<td>4.74</td>
<td>3.51</td>
</tr>
<tr>
<td>3.51</td>
<td>13.9</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Products [10(^{-9}) mol cm(^{-3})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>methylacetylene</td>
</tr>
<tr>
<td>(methylacetylene)(\mu)</td>
</tr>
<tr>
<td>59.9</td>
</tr>
<tr>
<td>(methylacetylene)/</td>
</tr>
<tr>
<td>(13.8)</td>
</tr>
<tr>
<td>1-pentene</td>
</tr>
<tr>
<td>8.05</td>
</tr>
<tr>
<td>cyclopentene</td>
</tr>
<tr>
<td>2.83</td>
</tr>
<tr>
<td>unidentified C(_5)’s</td>
</tr>
<tr>
<td>8.08</td>
</tr>
<tr>
<td>cyclopentadiene</td>
</tr>
<tr>
<td>7.71</td>
</tr>
<tr>
<td>2-methyl-1,4-pentadiene</td>
</tr>
<tr>
<td>13.5</td>
</tr>
<tr>
<td>biallyl</td>
</tr>
<tr>
<td>2.850</td>
</tr>
<tr>
<td>[biallyl](\mu)</td>
</tr>
<tr>
<td>(13.7)</td>
</tr>
<tr>
<td>4-methylenecyclopentene</td>
</tr>
<tr>
<td>29.3</td>
</tr>
<tr>
<td>3-methylenecyclopentene</td>
</tr>
<tr>
<td>143</td>
</tr>
<tr>
<td>unidentified C(_6)’s</td>
</tr>
<tr>
<td>65.2</td>
</tr>
<tr>
<td>(11—12 species)</td>
</tr>
</tbody>
</table>

| Allene balance [%] | 70 | 76 | 73 | 72 | 70 | 76 |

Allene concentration: 0.690×10\(^{-6}\) mol cm\(^{-3}\),
DAO concentration: 1.11×10\(^{-4}\) mol cm\(^{-3}\).

a) Values parenthesized represent the amounts of methyl-acetylene formed in the absence of DAO.

b) Values bracketed represent the estimated amounts\(\mu\) of biallyl formed by addition of the allyl radical to allene.
The scheme accounting for the formation of major allyl-addition products in these experiments is postulated as follows. It is based on a similar consideration described previously:\textsuperscript{8-13}:

\[
\begin{array}{c}
\text{RH} + \text{R}^* \rightarrow \text{RH} + \text{R}^* \\
\text{RH} + \text{R}^* \rightarrow \text{RH} + \text{R}^* \\
\end{array}
\]

In the scheme, RH is considered to be DAO which was present in the highest concentration (ca. 2.5 mol\%), and \( k_{\text{add}} \) represents a composite rate constant for addition of the allyl radical to allene. A certain amount of biallyl should be produced through the addition of the allyl radical to allene as seen in the scheme although almost all biallyl is produced by recombination of allyl radicals as described above. Although the amounts of biallyl produced through these two routes could not be measured separately, the amount of biallyl produced through the former route can be estimated. The amounts of biallyl evaluated by use of the ratio estimated previously\textsuperscript{14} to be 1.9, were listed together in brackets in Table 1.

The compounds listed in the table are believed to be produced by consumption of at least one molecule of allene. The total amounts of these products attained to more than 70% of the total amount of allene converted. Besides, allene is likely to be consumed by addition of the C\( _6 \) radical intermediates formed by the initial addition of the allyl radical, resulting in the formation of C\( _9 \) radicals or C\( _7-C_9 \) compounds which were not measured in the present experiments. Abstraction of hydrogen atom from allene by the allyl radical or from the allyl radical by allene is highly endothermic. In consideration of these possibilities, it is safe to assume that most of the allene converted was consumed by the initial addition of the allyl radical. Virtually, the conversion of allene, \( x \), fitted the first-order kinetics as shown in Fig. 1, where the results obtained at 430\( ^\circ \)C were excluded because the measurement of allene conversion (<1%) was in somewhat larger error. From Fig. 1, \( k'_{\text{add}} \) at each temperature was determined. By measurement of the initial slope of the formation curve of biallyl\textsuperscript{14}, \( \frac{d[biallyl]}{dt} \) in Eq. (4) at each temperature was obtained. The numerical value of \( k \) in Eq. (4) was available from the literature\textsuperscript{3,4,17,18}, as described above and settled to be \( 5 \times 10^{12} \text{cm}^3 \text{mol}^{-1} \text{s}^{-1} \), being regarded as independent of temperature. Table 2 illustrates the estimated concentration of the allyl radical. Figure 2 shows the temperature dependence of \( k_{\text{add}} \) thus obtained, which is formulated below:

\[
k_{\text{add}} = 10^{9.64}\exp(-23,100/RT) \text{cm}^3 \text{mol}^{-1} \text{s}^{-1}.
\]

The activation energy and the \( A \) factor evaluated for the elementary addition of the allyl radical to allene were ca. 23 kJ mol\(^{-1}\) and \( 10^{9.6} \text{cm}^3 \text{mol}^{-1} \text{ s}^{-1}\), respectively. These values obtained with allene are probably similar to those which may result with other unsaturated hydrocarbons, because it is suggested\textsuperscript{9,7} that kinetic parameters for addition of a certain radical to such unsaturated hydrocarbons as ethylene, propylene, acetylene, etc. are not largely different from each other. It should be noted that both values obtained here are

![Figure 1](attachment:image1.png) Application of First-order Kinetics to Allene Conversion

![Figure 2](attachment:image2.png) Temperature Dependence of Rate Constant for Addition of Allyl Radical to Allene

### Table 1 Estimated Concentration of Allyl Radicals in the Reaction System

<table>
<thead>
<tr>
<th>Temperature [( ^\circ )C]</th>
<th>Concentration\textsuperscript{a} [10(^{-11}) mol cm(^{-3})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>510</td>
<td>9.32</td>
</tr>
<tr>
<td>490</td>
<td>6.03</td>
</tr>
<tr>
<td>470</td>
<td>3.56</td>
</tr>
<tr>
<td>450</td>
<td>2.21</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Evaluated from biallyl formation rate\textsuperscript{14} and \( k_{\text{add}}\textsuperscript{8,9,17,18} \) by use of Eq. (4).
comparable to those\textsuperscript{19}-\textsuperscript{22} for addition of the ethyl or the propyl radical to ethylene. The present result implies that the allyl radical which is formed and to be added to allene, is not delocalized nor stabilized, because the energy of 40—50 kJ mol\textsuperscript{-1} is widely accepted as the allyl-resonance energy. Recently, it was reported\textsuperscript{20} again that the allyl-delocalization energy was ca. 60 kJ mol\textsuperscript{-1} which was deduced from the measurement of rotational barrier. Furthermore, the activation energy obtained is, surprisingly, smaller than 55—60 kJ mol\textsuperscript{-1} expected from the literature\textsuperscript{23}-\textsuperscript{25}. If these expected values involve an excess energy of 25 kJ mol\textsuperscript{-1} for partial destruction of allyl-resonance\textsuperscript{24}, the rest, \textit{i.e.}, 30—35 kJ mol\textsuperscript{-1} may be available for addition. Since $\Delta H$ of the reaction $\text{DAO} \rightarrow \text{allyl} + 2\text{CO}_2$, was estimated\textsuperscript{10} to be 125 kJ mol\textsuperscript{-1}, and since the activation energy obtained\textsuperscript{10} for DAO decomposition in the present experiments was 177 kJ mol\textsuperscript{-1}, ($177 - 125)/2 = 26$ kJ mol\textsuperscript{-1} may be permitted maximally as the excess energy for the nascent allyl radical. It is certain that the nascent allyl radical originated from pyrolysis of DAO can add to unsaturated hydrocarbons with the activation energy of 23 kJ mol\textsuperscript{-1} or so.

References

要 旨

アリルラジカルのアレンへの付加に対する活性化エネルギー

野原大輔，酒井和也

名古屋市立大学農学部，467 名古屋市瑞穂区田辺通 3-1

アリルラジカルがアレンに付加するため反応について，反応系中で同時進行するビアリルの生成を reference reaction として用い，速度解析を行った。実験は 450～510°C で，アリルラジカル生成源としてジェウ酸ジアリルを用い，常圧流通式反応器により行った。

得られた活性化エネルギーは 23 kJ·mol⁻¹，A factor は 10⁹ cm³·mol⁻¹·s⁻¹ であった。これらの値はエチルラジカルやプロピルラジカルがエチレンなどに付加する活性化パラメーターとよく類似している。得られた活性化エネルギーは，アリルラジカルの共鳴安定化を少なくとも部分的に破壊するためのエネルギーが上記のせられているはずとする様々な推定値とは異なったものである。本実験で生成したアリルラジカルのエネルギーレベルについて考察する。

Keywords
Allyl radical, Diallyl oxalate, Activation energy, Addition, Allene