Relative Rates of Bond Rotation and Ring Closure in the Photocycloaddition Intermediates from Fullerene-C60 and the Isomeric 2,4-Hexadienes

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Photocycloaddition of fullerene-C$_{60}$ to the isomeric 2,4-hexadienes reported by Orfanopoulos and co-workers gave a series of 2 + 2 cycloadducts in which bond rotation had occurred in some products. Relative rates of bond rotation and ring closure in the biradical intermediates were calculated from the product distributions using equations developed by Bartlett and co-workers. These data are reinterpreted to show that the ratio of the rate of bond rotation in the intermediate to the rate of ring closure to the cyclobutane product is ~70 for the trans-1-propenyl intermediate formed in the initial cis conformation. Data are inconsistent for the analogous cis-1-propenyl intermediate. The relative rate for the trans-1-propenyl intermediate formed in the initial trans conformation is ~9. Accurate relative rate determinations are highly dependent on very accurate product distribution determinations.

File list (1)

C60 + Hexadiene for ChemRxiv.pdf (4.63 MiB)
Relative Rates of Bond Rotation and Ring Closure in the Photocycloaddition

Intermediates from Fullerene-C\textsubscript{60} and the Isomeric 2,4-Hexadienes [1]

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Abstract:

Photocycloaddition of fullerene-C\textsubscript{60} to the isomeric 2,4-hexadienes reported by Orfanopoulos and co-workers gave a series of 2 + 2 cycloadducts in which bond rotation had occurred in some products. Relative rates of bond rotation and ring closure in the biradical intermediates were calculated from the product distributions using equations developed by Bartlett and co-workers. These data are reinterpreted to show that the ratio of the rate of bond rotation in the intermediate to the rate of ring closure to the cyclobutane product is \(~70\) for the \textit{trans}-1-propenyl intermediate formed in the initial \textit{cis} conformation. Data are inconsistent for the analogous \textit{cis}-1-propenyl intermediate. The relative rate for the \textit{trans}-1-propenyl intermediate formed in the initial \textit{trans} conformation is \(~9\). Accurate relative rate determinations are highly dependent on very accurate product distribution determinations.

**Keywords:** biradical; fullerene-C\textsubscript{60}; 2,4-hexadiene; photocycloaddition; rotation
**Introduction:**

Orfanopoulos and co-workers have studied extensively the photocycloaddition of fullerene-\(C_{60}\) (1) to various olefins [2-9]. These studies have delineated several aspects of these reactions including their stepwise nature and several other mechanistic details. One significant study involved the photocycloaddition of fullerene 1 to the three geometric isomers of 2,4-hexadiene (2) (Figure 1) [4]. From the product 4 distributions with the various isomers of the diene 2, the authors calculated for the proposed intermediate 3 a ratio of the rate of rotation about the bond that was originally a double bond in the diene 2 and the rate of ring closure of the intermediate 3. The present study reinterprets the reported data to give rate ratios that are different from the one reported.

![Figure 1. Probable partial mechanism of photocycloaddition of \(C_{60}\) to isomeric 2,4-hexadienes [4,8].](image)

**Discussion:**

The reaction conditions and product distributions are shown in Figure 2 [4].
Figure 2. Product distributions from photocycloaddition of C$_{60}$ to isomeric 2,4-hexadienes [4].
The cyclohexene derivative 10 was a thermal product from 1 and 5 [4]. One should note that the stereochemistry of the 1-propenyl groups was maintained in the reactions of 5 and 6 [4], and presumably 7. From these product distributions were calculated the percent of each intermediate, 13-16, that were converted to the cycloaddition products 8-9 and 11-12 [4] (Figure 3). One should also note that for the cis-1-propenyl intermediates 15 and 16, unexpectedly more cis-cyclobutane product 12 was formed from the initially formed trans-intermediate 15 than from the initially formed cis-intermediate 16.
The relative rates of rotation to ring closure were calculated by equations derived by Bartlett and co-workers [10] with a correction by Orfanopoulos and co-workers [4]. See the Supporting Information for details of the method and calculations. Using product distributions from trans,trans-diene 5 and the cis,cis-diene 6 Orfanopoulos and co-workers calculated $k_{\text{rot}}/k_{\text{clos}} = \sim 18$ [4]. Repeating this calculation gave 18.4 in agreement. However, as shown in Figure 4, this analysis requires intermediates 13 and
16 to be interconverted by rotation about a single bond, which cannot occur as 13 is a trans-1-propenyl intermediate and 16 is a cis-1-propenyl intermediate.

Two relative rates ($k_{rot}/k_{clos}$) ($k_1/k_2$ in Bartlett’s notation [10]) for the intermediates in these reactions can be calculated, one for the trans-1-propenyl intermediate 14 (Figure 5) and one for the cis-1-propenyl intermediate 16 (Figure 6).
Figure 5. Revised analysis of $k_{rot}/k_{clos}$ of trans-1-propenyl intermediates in photocycloaddition of C$_{60}$ to isomeric 2,4-hexadienes.
The distributions shown in Figure 5 for the trans-1-propenyl intermediates gave \( k_{\text{rot}}/k_{\text{clos}} = 71.4 \) while the distributions for the cis-1-propenyl intermediates gave \( k_{\text{rot}}/k_{\text{clos}} = -25.5 \), clearly an impossible situation, which is caused by the result noted above that more cis product is formed from the trans olefin than is formed from the cis olefin. Thus, a problem exists in some aspect of these reactions, possibly product identification and/or product distributions analysis.

In the Supporting Information are given calculated product distributions for the cis-propenyl products 11 and 12 if there was a 5.8% error in the analyses of these products. Using these product distributions would indicate that the closure of
intermediates 15 and 16 gave the products 11 and 12 in the same ratio (82.6:17.4), indicating that these intermediates were rotationally equilibrated before ring closure, i.e., a relatively small error in these analyses could account for the negative values for $k_{\text{rot}}/k_{\text{clos}}$. Thus, an accurate determination of $k_{\text{rot}}/k_{\text{clos}}$ is highly dependent on a very accurate product distribution determination.

The preceding calculations are for determining $k_{\text{rot}}/k_{\text{clos}}$ ($k_1/k_2$ in Bartlett’s notation [10]) for the initially formed cis intermediates 14 and 16. One can also calculate $k_{\text{rot}}/k_{\text{clos}}$ ($k_{-1}/k_3$ in Bartlett’s notation [10]) for the initially formed trans intermediates 13 and 15. The results of these calculations gave 9.19 for the trans-1-propenyl intermediate 13 and –5.74 for the cis-1-propenyl intermediate 15. Thus, as expected, if $k_{\text{clos}}$ is similar for both the initially formed cis 14 and trans 13 intermediates, the cis intermediate rotates faster than the trans intermediate, presumably for steric reasons.

In Bartlett and co-workers original paper [10] on the thermal cycloaddition of 1,1-dichloro-2,2-difluoroethylene to the isomeric 2,4-hexadienes, 5-7, the values of p and q (see Supporting Information for definitions of p and q) were similar for the cis-1-propenyl and trans-1-propenyl (R in Bartlett’s notation [10]) biradical intermediates. The parameters p and q are ratios of cis and trans cyclobutyl products starting from the cis and trans olefins and are also ratios of various rate constants for interconversion of the cis and trans rotamers ($k_1$ and $k_{-1}$) and for ring closures ($k_2$ and $k_3$),

$$ p = \frac{k_2(k_{-1} + k_3)}{k_1k_3}, \quad q = \frac{k_3(k_1 + k_2)}{k_{-1}k_2} $$

(see Supporting Information for explicit definitions). Bartlett and co-workers [10] calculated average vales of p and q and thus
average values of $k_{\text{rot}}/k_{\text{clos}}$ (or the inverse). In the reaction of $C_{60}$ (1) with the dienes 5-7 the values of $p$ and $q$ differ significantly: $p = 0.188$, $q = 4.23$ for the cis-1-propenyl; $p = 0.143$, $q = 7.89$ for trans-1-propenyl) and using average values seems unwarranted. Thus, values for $k_{\text{rot}}/k_{\text{clos}}$ differ for the cis-1-propenyl and trans-1-propenyl biradicals according to the reported data [4].

The negative values of $k_{\text{rot}}/k_{\text{clos}}$ for the cis-1-propenyl biradical may be caused by errors in product identification or in quantitative analysis or the mechanism may be more complicated than a simple formation of biradical intermediates that can rotate before ring closure (like some concerted suprafacial, antarafacial 2 + 2 cycloaddition).

**Conclusion:**

Data reported by Orfanopoulos and co-workers for the photocycloaddition of fullerene-$C_{60}$ to the isomeric 2,4-hexadienes have been reinterpreted to show that the ratio of the rate of bond rotation in the intermediate to the rate of ring closure to the cyclobutane product is $\sim$70 for the trans-1-propenyl intermediate formed in the initial cis conformation. Reported data have been shown to be inconsistent for the analogous cis-1-propenyl intermediate for a simple biradical mechanism. The relative rate for the trans-1-propenyl intermediate formed in the initial trans conformation is $\sim$9. Accurate relative rate determinations are highly dependent on very accurate product distribution determinations.

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Supporting Information

Relative Rates of Bond Rotation and Ring Closure in the Photocycloaddition Intermediates from Fullerene-C_{60} and the Isomeric 2,4-Hexadienes

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Relative Rates of Rotation and Closure of Diradicals

\[ \text{Relative Rates of Rotation and Closure of Diradicals} \]

[Chemical structures and reactions]

\[ + \rightarrow \text{R} \]

\[ \text{(z)} \quad \text{R}^{\text{R}} \quad \text{k}_1 \quad \text{k}_\text{eq} \quad \text{(w)} \quad \text{R}^{\text{R}} \]

\[ \text{R}^{\text{R}} \quad \text{(x)} \]

\[ \text{R}^{\text{R}} \quad \text{(y)} \]

Montgomery, L. K.; Schueler, K. E.; Bartlett, P. D. J. Am. Chem. Soc. 1964, 86, 622-628.
Kinetic Analysis

Definitions: 
- \( k_1 \) (closure), \( k_2 \) (rotation), \( a = k_1 - k_2 \), \( b = k_1 \)

\[
\begin{align*}
\frac{d[\text{cis}]}{dt} &= k_2 [\text{cis}] - (k_1 + k_3) [\text{cis}] = 0 \\
\frac{d[\text{trans}]}{dt} &= k_3 [\text{trans}] - (k_1 + k_2) [\text{trans}] = 0 \\
\frac{d[\text{cis}]}{dt} &= k_2 [\text{cis}] - (k_1 + k_3) [\text{cis}] = 0 \\
\frac{d[\text{trans}]}{dt} &= k_3 [\text{trans}] - (k_1 + k_2) [\text{trans}] = 0
\end{align*}
\]

\[
\begin{align*}
p &= a + b \\
q &= a (1 + b) \\
\sigma &= \frac{P + 1}{Q + 1} \\
b &= q + 1
\end{align*}
\]

\[
\begin{align*}
k_{\text{cis}} &= \frac{a (1 + b)}{b} \\
k_{\text{trans}} &= \frac{a}{b + 1} \\
k_{\text{trans}} &= \frac{a (1 + b)}{b}
\end{align*}
\]

\[
\begin{align*}
k_{\text{cis}} &= \frac{a (1 + b)}{b} \\
k_{\text{trans}} &= \frac{a}{b + 1} \\
k_{\text{trans}} &= \frac{a (1 + b)}{b}
\end{align*}
\]

Montgomery, L. K.; Schaufler, K. E.; Barlett, P. D. J. Am. Chem. Soc. 1964, 86, 622-628.
Original Analysis of $k_{\text{rot}}/k_{\text{clos}}$

\[ p = \frac{\text{cis}}{\text{trans}_{\text{cis}}} = \frac{15.8}{84.2} = 0.188 \]

\[ q = \frac{\text{trans}}{\text{cis}_{\text{trans}}} = \frac{88.7}{11.3} = 7.89 \]

\[ \frac{k_{\text{rot}}}{k_{\text{clos}}} = \frac{q + 1}{pq - 1} = \frac{7.89 + 1}{(0.188)(7.89) - 1} = 18.4 \quad \text{(Authors reported ~18)} \]

Vassilikogiannakis, G.; Chronakis, N.; Orfanopoulos, M. J. Am. Chem. Soc. 1998, 120, 9911-9920.
Revised Analysis of $k_{rot}/k_{clos}$ for trans-1-Propenyl Products

\[ p = \frac{\text{cis}}{\text{trans}} = \frac{12.5}{87.5} = 0.143 \]
\[ q = \frac{\text{trans}}{\text{cis}} = \frac{88.7}{11.3} = 7.89 \]

\[ \frac{k_{rot}}{k_{clos}} = \frac{q + 1}{pq - 1} = \frac{7.89 + 1}{(0.143)(7.89) - 1} = 71.4 \]
Revised Analysis of $k_{rot}/k_{clos}$ for cis-1-Propenyl Products

\[ p = \frac{\text{cis}}{\text{trans}} \frac{15.8}{84.2} = 0.188 \quad q = \frac{\text{trans}}{\text{cis}} \frac{80.9}{19.1} = 4.23 \]

\[ \frac{k_{rot}}{k_{clos}} = \frac{q + 1}{pq - 1} = \frac{4.23 + 1}{(0.188)(4.23) - 1} = -25.5 \text{ (Not possible)} \]
New Analysis of $k_{rot}/k_{clos}$ for trans-1-Propenyl Products

\[
p = \frac{\text{cis}}{\text{trans}} \left(\begin{array}{c}
\text{cis} \\
\text{trans}
\end{array}\right) = \frac{12.5}{87.5} = 0.143
\]

\[
q = \frac{\text{trans}}{\text{cis}} \left(\begin{array}{c}
\text{trans} \\
\text{cis}
\end{array}\right) = \frac{88.7}{11.3} = 7.89
\]

\[
\frac{k_{rot}}{k_{clos}} = \frac{p + 1}{pq - 1} = \frac{0.143 + 1}{(0.143)(7.89) - 1} = 9.18
\]
New Analysis of $k_{rot}/k_{clos}$ for cis-1-Propenyl Products

\[
p = \frac{\text{cis}}{\text{trans}} = \frac{15.8}{84.2} = 0.188 \quad q = \frac{\text{trans}}{\text{cis}} = \frac{89.9}{19.1} = 4.23
\]

\[
\frac{k_{rot}}{k_{clos}} = \frac{p + 1}{pq - 1} = \frac{0.188 + 1}{(0.188)(4.23) - 1} = -5.74 \text{ (Not possible)}
\]
trans-trans- and cis-cis-2,4-Hexadienes with 5.8% Error in Product Distribution

\[
\begin{align*}
\text{C}_6\text{O} & \quad + \quad \text{vinyl} \\
(0.7-0.9 \text{ mM}) & \quad (80 \times \text{excess}) \\
(33\% \text{ conversion}) & \quad \xrightarrow{\text{hv \ 300 W Xe lamp}} \quad \text{products} \\
\text{PhMe, Ar} & \quad \sim 5^\circ \text{C, 20 min} \\
(69.4\%) & \quad (8.8\%) \quad (21.8\%) \\
\text{(thermal product)} & \quad (+2\% \text{ of recovered diene})
\end{align*}
\]

\[
\begin{align*}
\text{C}_6\text{O} & \quad + \quad \text{vinyl} \\
(0.7-0.9 \text{ mM}) & \quad (80 \times \text{excess}) \\
(43\% \text{ conversion}) & \quad \xrightarrow{\text{hv \ 300 W Xe lamp}} \quad \text{products} \\
\text{PhMe, Ar} & \quad \sim 5^\circ \text{C, 20 min} \\
(84.2\%) & \quad [5.8\%] \quad (15.8\%) \\
[79.3\%] & \quad (+5.8\%) \quad (-4\% \text{ of recovered diene})
\end{align*}
\]
**cis-trans-2,4-Hexadiene**

with 5.8% Error in Product Distribution

\[ \text{C}_6\text{H}_{12} + \text{C}_6\text{H}_{12} \xrightarrow{hv \text{ 300 W Xe lamp}} \text{Product mixture} \]

PhMe, Ar

\(-5^\circ\text{C}, 20\) min

(51.9%)

(7.4%)

(31.7% + [5.6%] = 33.5%)

(7.5% - [5.8%] = 7.1%)

(probably thermal product from trans-trans-diene formed in reaction)

(~3% of recovered diene) (1% of recovered diene)
Product Sources in Photocycloaddition to 2,4-Hexadienes with 5.8% Error in Product Distributions

Cis propenyl intermediates rotationaly equilibrated before ring closure
Comparison of $k_{\text{rot}}/k_{\text{clos}}$ for cis and trans Diradicals

\[
\frac{k_{\text{rot}}}{k_{\text{clos}}} = -70
\]

\[
\frac{k_{\text{rot}}}{k_{\text{clos}}} = -9
\]
