**Stoichiometry of the decomposition reaction of the diazene**

The stoichiometric analysis to infer the proportion of combination and disproportionation reactions in the encounter of two BME· radicals and in the encounter between BME· and t-Bu· radicals is based on the product distribution of the steady state photolysis of the symmetric ketone (2,4-bis-biphenyl-4-yl-2,4-dimethyl-pentan-2-one) and of (1-biphenyl-4-yl-1-methyl-ethyl)-tert-butyl diazene. The name of the compounds and the reactions in which they are formed is based on Scheme 2.

The product distribution in the photolysis of the symmetric ketone yields directly the ratio between combination and disproportionation reactions of BME· radicals. After evaluation of several experiments with ketone conversion between 10 to 20 % this value, that we call $\beta$, was found to be $0.14 \pm 0.01$, meaning combination occurs about 7 times more often than disproportionation.

We also make the reasonable assumption that out-of-cage encounters between BME· and t-Bu· should double the encounters between BME· radicals.

This stoichiometric analysis does not take into account the butanes produced in the reaction of the diazene, as they are not detected in our work.

To estimate the cage factor it is necessary to distinguish between products formed in the geminate cage from products originated from diffusive encounters.

- **biBME$_{2}$BB**: produced out-of-cage by combination of two BME· radicals
- **TMPBiAB**: TMPB produced in-cage
- **TMPBoAB**: TMPB produced out-of-cage by combination after diffusive encounters between A and B
- **i-PBiAB**: produced in-cage by disproportionation between BME· and t-Bu·
- **i-PB$_{0}$AB**: produced out-of-cage by disproportionation of BME· and t-Bu·
- **i-PB$_{0}$BB**: produced out-of-cage by disproportionation of two BME· radicals
i-PenBiAB: produced in-cage by disproportionation between BME- and t-Bu-
i-PenBoAB: produced out-of-cage by disproportionation of BME- and t-Bu-
i-PenBoBB: produced out-of-cage by disproportionation of two BME- radicals

To determine these eight unknowns, we count on measurements of four products (biBME, TMPB, i-PenB and i-PB) and the following eight equations:

\[ i\text{-PenB} = i\text{-PenBiAB} + i\text{-PenBoAB} + i\text{-PenBoBB} \]  
(1)

is the mass conservation of \( i\text{-PenB} \)

\[ i\text{-PB} = i\text{-PBiAB} + i\text{-PBoAB} + i\text{-PBoBB} \]  
(2)

is the mass conservation of \( i\text{-PB} \)

\[ \text{TMPB} = \text{TMPBiAB} + \text{TMPBoAB} \]  
(3)

is the mass conservation of TMPB

\[ 2 \times (i\text{-PBoBB} + bi\text{BME}_{oBB}) = i\text{-PenB}_{oAB} + i\text{-PBoAB} + \text{TMPBoAB} \]  
(4)

expresses the fact that total encounters of BME- and t-Bu- radicals doubles those of two BME- radicals

\[ i\text{-PBoBB} = i\text{-PenB}_{oBB} \]  
(5)

is deduced from the fact that the only source of \( i\text{-PB} \) is disproportionation of two BME- radicals

\[ \frac{i\text{-PenBiAB}}{\text{TMPBiAB}} = \frac{i\text{-PenBoAB}}{\text{TMPBoAB}} \]  
(6)

\[ \frac{i\text{-PBiAB}}{\text{TMPBiAB}} = \frac{i\text{-PBoAB}}{\text{TMPBoAB}} \]  
(7)

express the fact that product relation of encounters of BME- and t-Bu- radicals is equal in diffusive and in geminate encounters.

Finally:

\[ i\text{-PenB}_{oBB} = i\text{-PBoBB} = \beta \times bi\text{BME}_{oBB} \]  
(8)
provides the ratio of combination and disproportionation products from encounters of BME-radicals and this ratio is obtained from the photolysis of the symmetric ketone (equation (5) is contained in this equality).

These eight equations allow us to calculate the eight unknown quantities $i$-PenB$_{iAB}$, $i$-PB$_{iAB}$, TMPB$_{iAB}$, $i$-PenB$_{oAB}$, $i$-PenB$_{oBB}$ $i$-PB$_{oAB}$, $i$-PB$_{oBB}$ and TMPB$_{oAB}$ by knowing the yield fractions of $i$-PenB, $i$-PB, biBME and TMPB.

To find individual amounts (in yield fraction) we replace equations (1), (2), (3), (5) and (8) into equation (4) to obtain:

$$(2 + 4 \times \beta) \times \text{biBME}_{oBB} = \text{TMPB} + i$\text{-PB} + i$$\text{-PenB} - (i$$\text{-PenB}_{iAB} + i$\text{-PB}_{iAB} + TMPB$_{iAB}$) \quad (9)$$

If we replace (2), (3) and (8) into (6) we get:

$$\frac{i$\text{-PenB}_{iAB}}{\text{TMPB}_{iAB}} = \frac{i$\text{-PB} - i$\text{-PenB}_{iAB} - \beta \times \text{biBME}_{oBB}}{\text{TMPB} - \text{TMPB}_{iAB}} \quad (10)$$

that subsequently gives:

$$\frac{i$\text{-PenB}_{iAB}}{\text{TMPB}_{iAB}} = \frac{i$\text{-PenB} - \beta \times \text{biBME}_{oBB}}{\text{TMPB}} \quad (11)$$

In a similar way, we obtain the relation between $i$-PB$_{iAB}$ and TMPB$_{iAB}$ by replacing equations (1), (3), (5) and (8) into (7):

$$\frac{i$\text{-PB}_{iAB}}{\text{TMPB}_{iAB}} = \frac{i$\text{-PB} - \beta \times \text{biBME}_{oBB}}{\text{TMPB}} \quad (12)$$

If we now replace (11) and (12) into (9) we obtain an equation where TMPB$_{iAB}$ is the only unknown and regrouping:

$$\text{TMPB}_{iAB} = \text{TMPB} \times \frac{(\text{TMPB} + i$\text{-PB} + i$\text{-PenB}) - (2 + 4 \times \beta \times \text{biBME}_{oBB})}{(\text{TMPB} + i$\text{-PB} + i$\text{-PenB}) - 2 \times \text{biBME}_{oBB}} \quad (13)$$

The solved equations for the other values are thus:

$$i$\text{-PB}_{oBB} = \beta \times \text{biBME}_{oBB}$$

$$i$\text{-PenB}_{oBB} = \beta \times \text{biBME}_{oBB}$$

both already known from equation (8)
\[ i - \text{PenB}_{iAB} = (i - \text{PenB} - \beta \times \text{biBME}_{oBB}) \times \frac{\text{TMPB}_{iAB}}{\text{TMPB}} \]

\[ i - \text{PB}_{iAB} = (i - \text{PB} - \beta \times \text{biBME}_{oBB}) \times \frac{\text{TMPB}_{iAB}}{\text{TMPB}} \]

from equations (11) and (12) respectively, and

\[ \text{TMPB}_{oAB} = \text{TMPB} - \text{TMPB}_{iAB} \]

\[ i - \text{PB}_{oAB} = i - \text{PB} - i - \text{PB}_{iAB} - i - \text{PB}_{oBB} \]

\[ i - \text{PenB}_{oAB} = i - \text{PenB} - i - \text{PenB}_{iAB} - i - \text{PenB}_{oBB} \]

from the mass conservation equations.