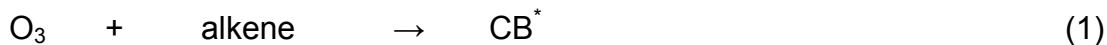
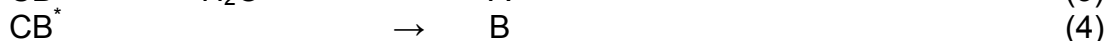


Inspection of a reputable dictionary informs us that the word 'Absurd' means utterly or obviously senseless, illogical, or untrue; contrary to all reason or common sense; laughably foolish or false. Rather a strong word to use one would suggest in a review. Let us see whether this word is appropriate. Let us consider another limiting system where ozonolysis of an alkene only produces excited ('hot') criegee biradicals (CB^*), denoted by reaction (1).



These 'hot' CB^* can then either be quenched in reaction (2) by H_2O to form 'cold' CB or decompose to form products B in reaction (4), whilst 'cold' CB can react with H_2O to form product A in reaction (3).



$$\frac{d[CB^*]}{dt} = k_1[O_3][alkene] - k_2[CB^*][H_2O] - k_4[CB^*] \quad \text{I}$$

$$\text{Assuming the steady state approximation } [CB^*] = \frac{k_1[O_3][alkene]}{k_2[H_2O] + k_4} \quad \text{II}$$

$$\frac{d[CB]}{dt} = k_2[CB^*][H_2O] - k_3[CB][H_2O] \quad \text{III}$$

$$\text{Assuming the steady state approximation } [CB] = \frac{k_2[CB^*]}{k_3} \quad \text{IV}$$

$$\frac{d[A]}{dt} = k_3[CB][H_2O] = \frac{k_3 k_2 [CB^*][H_2O]}{k_3} = k_2[CB^*][H_2O] = \frac{k_2 k_1 [O_3][alkene][H_2O]}{k_2[H_2O] + k_4} \quad \text{V}$$

$$\frac{d[B]}{dt} = k_4[CB^*] = \frac{k_4 k_1 [O_3][alkene]}{k_2[H_2O] + k_4} \quad \text{VI}$$

Combining V and VI

$$\frac{d[A]}{d[B]} = \frac{k_2 k_1 [O_3][alkene][H_2O]}{k_2[H_2O] + k_4} \times \frac{k_2[H_2O] + k_4}{k_4 k_1 [O_3][alkene]} = \frac{k_2[H_2O]}{k_4} \quad \text{VII}$$

$$\text{If we wish to look at the yield of A, one could look at } yield(A) = \frac{\frac{d[A]}{dt}}{\frac{d[B]}{dt} + \frac{d[A]}{dt}} \quad \text{VIII}$$

and this gives the yield (A) = $\frac{k_2[H_2O]}{k_2[H_2O] + k_4}$

The analysis is valid, yes the k_2 is associated with quenching and not bimolecular reaction but we do not need to distinguish between 'hot' and 'cold', whatever definition J.-F. Muller is using, just the fraction that decomposes as a function of $[H_2O]$. As $[H_2O]$ increases so more CB^* is quenched and more A can be formed from reaction (3), the approximation is far from absurd.