Calculations

Homodesmotic Reactions (RC4)

Let us first analyze the homodesmotic class of reactions, RC4. According to Wheeler, Houk, Schleyer, and Allen (WHSA) [1] these reactions are required to preserve (a) the numbers of each type of carbon-carbon bond (Csp^3-Csp^3, Csp^3-Csp^2, Csp^3-Csp, Csp^2-Csp^2, Csp^2-Csp, Csp-Csp,Csp^2=Csp^2, Csp=Csp, Csp=Csp, Csp≡Csp) in reactants and products, and (b) the numbers of each type of carbon atom (sp^3, sp^2, sp) with zero, one, two, and three hydrogens attached in reactants and products. This definition should be amended with an additional condition that distinguishes among two different carbon atoms in sp hybridization state, i.e., carbon atoms in acetylene and allene. We, thus have a total of 20 groups labeled g_1, g_2,…,g_{20} and presented in Table 1. Notice that the carbon atom in molecules like allene is presented as a group =C= (g_{18}). The n = 16 reference species employed by WHSA are labeled A_1, A_2,…,A_{16} and are presented in Scheme 1. Consider, next the group matrix

g_1	g_2	g_3	g_4	g_5	g_6	g_7	g_8	g_9	g_{10}	g_{11}	g_{12}	g_{13}	g_{14}	g_{15}	g_{16}	g_{17}	g_{18}	g_{19}	g_{20}	
1	0	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	A_1
0	0	0	0	0	0	1	0	0	0	0	0	0	0	2	0	0	0	0	0	A_2
0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	2	0	A_3
2	0	0	0	0	0	0	0	0	0	2	1	0	0	0	0	0	0	0	0	A_4
0	1	0	0	0	0	1	0	0	0	1	0	0	0	1	1	0	0	0	0	A_5
0	0	1	0	0	0	0	0	0	1	1	0	0	0	0	0	0	0	1	1	A_6
0	0	0	0	0	0	0	2	0	0	0	0	0	0	2	0	0	1	0	0	A_7
3	0	0	0	0	0	0	0	0	0	3	0	1	0	0	0	0	0	0	0	A_8
0	2	0	0	0	0	1	0	0	0	2	0	0	0	1	0	1	0	0	0	A_9
4	0	0	0	0	0	0	0	0	0	4	0	0	1	0	0	0	0	0	0	A_{10}
0	0	0	1	0	0	2	0	0	0	0	0	0	0	2	2	0	0	0	0	A_{11}
0	0	0	0	1	0	1	0	0	1	0	0	0	0	1	1	0	0	1	1	A_{12}
0	0	0	0	0	1	0	0	0	2	0	0	0	0	0	0	0	0	2	2	A_{13}
0	0	0	0	0	0	0	2	1	0	0	0	0	0	2	0	0	2	0	0	A_{14}
0	1	0	1	0	0	2	0	0	0	1	0	0	0	2	1	1	0	0	0	A_{15}
0	1	0	0	1	0	1	0	0	1	1	0	0	0	1	0	1	0	1	1	A_{16}

After a series of elementary column operations this matrix may be brought to the following form

1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0	0	0	0	0
0	0	0	0	-1	0	0	0	1	0	1	0	0	0	0	0	0	0	0	0
0	0	0	0	-1	0	0	0	1	0	0	1	0	0	0	0	0	0	0	0

It immediately follows that the rank of the group matrix is equal to $q = 14$. Thus, the number of linearly independent reactions is $m = n - q = 2$. According to the GA RERs formalism, these reactions are

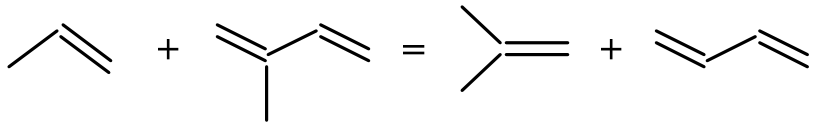
$$\begin{vmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_1 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_2 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_3 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_4 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_5 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_6 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_7 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & A_8 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & A_9 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & A_{10} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & A_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & A_{12} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & A_{13} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & A_{14} \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & A_{15} \end{vmatrix}$$

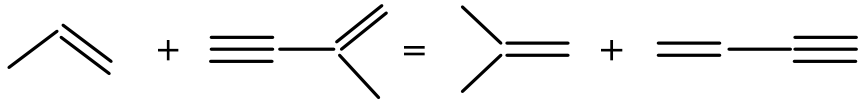
$$= A_5 - A_9 - A_{11} + A_{15} = 0$$

$$\begin{vmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_1 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_2 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_3 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_4 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_5 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_6 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_7 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & A_8 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & A_9 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & A_{10} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & A_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & A_{12} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & A_{13} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & A_{14} \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & A_{16} \end{vmatrix}$$

$= A_5 - A_9 - A_{12} + A_{16} = 0$

To facilitate the visualization of the group balance, let us also present the reactions in a more conventional format





This simple exercise shows that the RC4 class of reactions is not unique. Concomitantly, it shows that a unique RC4 reaction may be generated in several ways by discarding two species from the list A_5, A_9, A_{11}, A_{12}, A_{15} and A_{16}. Indeed, according to the above definition a reaction is unique if it involves no more than $q + 1 = 14 + 1 = 15$ species. One of these species is the hydrocarbon **A** for which we seek a RC4 reaction while the remaining 14 species are selected from the list of reference species A_1 - A_{16}.

To illustrate the procedure, let us generate two unique RC4 reactions. The first one is obtained by discarding the last two species, A_{15} and A_{16}. In this case, any conceivable hydrocarbon **A** can be "build" from the first fourteen reference species A_1, A_2,…,A_{14}. Because the rank of the group matrix is equal to $q = 14$, it follows that 6 groups out of 20 are linearly dependent. Removing these groups or, alternatively the respective columns from the group matrix will not change its rank. For instance, removing the columns g_1, g_2, g_3, g_8, g_{17} and g_{20} from the group matrix does not change its rank. Let n_1, n_2,…,n_{20} be the number of groups g_1, g_2,…, g_{20} in species **A**. Then, the general equation of the RC4 reaction involving the first fourteen species A_1, A_2,…,A_{14} is

$$
\begin{vmatrix}
0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & A_1 \\
0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 0 & 0 & A_2 \\
0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & A_3 \\
0 & 0 & 0 & 0 & 0 & 0 & 2 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & A_4 \\
0 & 0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & A_5 \\
0 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & A_6 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 1 & 0 & A_7 \\
0 & 0 & 0 & 0 & 0 & 0 & 3 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & A_8 \\
0 & 0 & 0 & 1 & 0 & 0 & 2 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & A_9 \\
0 & 0 & 0 & 0 & 0 & 0 & 4 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & A_{10} \\
1 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & 2 & 0 & 0 & A_{11} \\
0 & 1 & 0 & 1 & 0 & 1 & 0 & 0 & 0 & 0 & 1 & 1 & 0 & 1 & A_{12} \\
0 & 0 & 1 & 0 & 0 & 2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 2 & A_{13} \\
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 2 & 0 & 2 & 0 & A_{14} \\
n_4 & n_5 & n_6 & n_7 & n_9 & n_{10} & n_{11} & n_{12} & n_{13} & n_{14} & n_{15} & n_{16} & n_{18} & n_{19} & \mathbf{A}
\end{vmatrix}
$$

$$
= -2\mathbf{A} - (-2n_4 - 2n_5 - 2n_6 + 4n_7 - 4n_9 + 2n_{10} - n_{11} + 2n_{12} + 3n_{13} + 4n_{14} - 2n_{15} - n_{16} + 4n_{18} - n_{19})A_1 - 2(n_7 - 2n_9 - n_{15} + 2n_{18})A_2 - 2(n_{10} - n_{19})A_3 + 2n_{12}A_4 - 2(2n_4 + n_5 - n_{16})A_5 - 2(n_5 + 2n_6 - 2n_{10} + n_{19})A_6 - 2(2n_9 - n_{18})A_7 - 2n_{13}A_8 - 2(-2n_7 + 2n_9 + n_{15} + n_{16} - 2n_{18})A_9 + 2n_{14}A_{10} + 2n_4A_{11} + 2n_5A_{12} + 2n_6A_{13} + 2n_9A_{14} = 0
$$

Based on this equation it may be concluded that the stoichiometric coefficients of the species A_1, A_2, A_3, A_5, A_6, A_7 and A_9 may take in principle both positive and negative values. In WHSA's terminology it means that these species can be both elemental reactants and elemental products. On the other hand, the stoichiometric coefficients of the species A_4, A_{10}, A_{11}, A_{12}, A_{13} and A_{14} can take only positive values and, hence, can be only elemental products (providing the species A is a product in the reaction). For illustration purposes consider the RC4 reaction for buckminsterfullerene C_{60}. For this species we have $n_4 = 60$, $n_7 = 30$, $n_{17} = 60$ while the number of all other groups is equal to zero. This gives

$$C_{60} + 30A_2 + 120A_5 = 60A_9 + 60A_{11}$$

It is seen that this reaction follows the WHSA partition of the reference species into elemental reactants and products.

A different RC4 reaction may be obtained by eliminating, for instance, species A_5 and A_{11}. In this case, any conceivable hydrocarbon **A** may be "build" from the remaining fourteen species as follows

$$- 2\mathbf{A} - (-2n_4 - 2n_5 - 2n_6 + 4n_7 - 4n_9 + 2n_{10} - n_{11} + 2n_{12} + 3n_{13} + 4n_{14} - 2n_{15} - n_{16} + 4n_{18} - n_{19})A_1 - (2n_7 - 4n_9 - 2n_{15} + 4n_{18})A_2 - 2(n_{10} - n_{19})A_3 + 2n_{12}A_4 - 2(n_5 + 2n_6 - 2n_{10} + n_{19})A_6 - 2(2n_9 - n_{18})A_7 + 2n_{13}A_8 - 2(2n_4 + n_5 - 2n_7 + 2n_9 + n_{15} - 2n_{18})A_9 + 2n_{14}A_{10} - 2(n_4 - n_{16})A_{12} + 2n_6A_{13} + 2n_9A_{14} + 2n_4A_{15} - 2(- n_4 - n_5 + n_{16})A_{16} = 0$$

It may be noticed in this case the partition of the reference species into elemental reactants and elemental products is problematic. As an example, consider the RC4 reaction for C_{60} for this selection of reference species

$$C_{60} + 30A_2 + 60A_9 + 60A_{12} = 60A_{15} + 60A_{16}$$

As can be seen, the species A_9 and A_{12} are now elemental reactants and, hence, the WHSA partition of the reference species into elemental reactants and products is not valid any more. At a first glance the above RC4 reaction for C_{60} is odd in that in involves reference species that do not match the groups present in C_{60}. However, this reaction preserves what is supposed to preserve and as such, is a legitimate RC4 reaction.

"Old" Hyperhomodesmotic Reactions (RC5)

To distinguish between the RC5 reaction proposed by WHSA and Wodrich, Corminboeuf and Wheeler (WCW) [2] in what follows we will refer to "old" RC5 and "new" RC5 respectively. Consider first the stoichiometric uniqueness as applied to the "old" definition of hyperhomodesmotic reactions proposed by WHSA. According to WHSA, an "old" RC5 reaction preserves (a) the numbers of carbon-carbon bond types $H_3C\text{-}CH_2$, $H_3C\text{-}CH$, $H_2C\text{-}CH_2$, $H_3C\text{-}C$, $H_2C\text{-}CH$, $H_2C\text{-}C$, HC-CH, HC-C, C-C, $H_2C{=}CH$, HC=CH, $H_2C{=}C$, HC=C, C=C, HC≡C, and C≡C, and (b) the numbers of each type of carbon atom (sp^3, sp^2, sp) with zero, one, two, and three hydrogens attached, i.e., $CH_3(sp^3)$, $CH_2(sp^3)$, $CH(sp^3)$, $C(sp^3)$, $CH_2(sp^2)$, $CH(sp^2)$, $C(sp^2)$, CH(sp) and C(sp). Again, it is necessary to distinguish between the C(sp) atom in species like acetylene and

allene derivatives. Thus, we have a total of 26 groups and n = 34 species. The list of groups labeled g_1, g_2,…,g_{26} is presented in Table 2 while the list of species labeled B_1, B_2,…,B_{34} is presented in Scheme 2. Now, it can be easily checked that the rank of the group matrix is equal to q = 17. In other words, only 17 groups from a total of 26 are linearly independent. Moreover, it can be readily checked that the first 17 groups are linearly independent. Thus, the number of independent reactions m is equal to $m = n - q$ = 34 - 17 = 17. Three important consequences follow directly from this result. First, we have 17 linearly independent reactions among the 34 reference species and not 12 as stipulated by WCW. As an example, we present below an arbitrarily selected set

$$-B_2 + B_4 - B_9 + B_{18} = 0$$

$$-B_5 + B_6 - B_{10} + B_{19} = 0$$

$$-B_2 + B_4 - B_{11} + B_{20} = 0$$

$$-B_5 + B_6 - B_{12} + B_{21} = 0$$

$$-B_2 + B_4 - B_{12} + B_{22} = 0$$

$$-B_5 + B_6 - B_{13} + B_{23} = 0$$

$$B_5 - B_7 - B_{15} + B_{24} = 0$$

$$-B_3 + B_6 - B_{10} + B_{25} = 0$$

$$-B_3 + B_6 - B_{12} + B_{26} = 0$$

$$-B_3 + B_6 - B_{13} + B_{27} = 0$$

$$2B_5 - 2B_7 - B_{16} + B_{28} = 0$$

$$-2B_2 + 2B_4 - B_{11} + B_{29} = 0$$

$$-B_2 - B_3 + B_4 + B_6 - B_{12} + B_{30} = 0$$

$$-2B_3 + 2B_6 - B_{13} + B_{31} = 0$$

$$-B_2 + B_4 - B_5 + B_6 - B_{12} + B_{32} = 0$$

$$-B_3 - B_5 + 2B_6 - B_{13} + B_{33} = 0$$

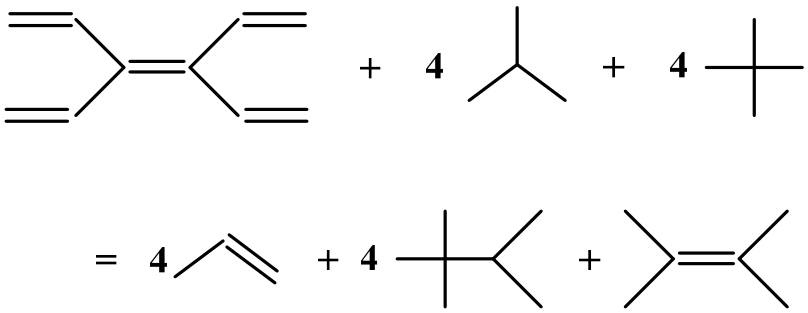
$$-2B_5 + 2B_6 - B_{13} + B_{34} = 0$$

Second, in defining the “old” RC5 it is not necessary to specify condition (b), i.e., the numbers of each type of carbon atom in various hybridization states. This information is simply redundant. Third, and most importantly, the “old” RC5 reactions should not be discarded because they are not unique or because certain fine structural aspects are not met. Just like any other type of reactions, such as isodesmic or homodesmotic, the “old”

RC5 reactions are legitimate. Rather, the problem is the WCW inability to generate a unique "old" RC5 reaction. Based on our analysis, we conclude that a single/unique RC5 reaction should not involve more than $n = q + 1 = 17 + 1 = 18$ species. Namely, one of these species should be the hydrocarbon **B** for which we seek a RC5 reaction while the remaining 17 species may be selected from the list of 34 reference species. In particular, an appropriate selection are the first 17 reference species in Scheme 2 (this is reason we have reordered the list of species). Following the same procedure illustrated above for RC4 reactions, it may be shown that the general equation of the "old" RC5 reaction involving the first 17 reference species is

$$- 12\mathbf{B} + 6(n_1 - 2n_4 - n_5 - n_6)B_1 + 12n_{10}B_2 + 12n_{15}B_3 + 4(n_2 - 2n_5 - 8n_7 - 4n_8 - 2n_{10} - 4n_{12} - 2n_{13})B_4 + 12(n_{11} - 2n_{17})B_5 - 3(-n_3 + 3n_6 + 3n_8 + 6n_9 + 2n_{11} + 2n_{13} + 4n_{14} + n_{15} + 2n_{16} - 4n_{17})B_6 + 12n_{17}B_7 + 12n_4B_8 + 12n_5B_9 + 12n_6B_{10} + 12n_7B_{11} + 12n_8B_{12} + 12n_9B_{13} + 12n_{12}B_{14} + 12n_{13}B_{15} + 12n_{14}B_{16} + 12n_{16}B_{17} = 0$$

This general equation points to another discrepancy in the WHSA approach. Namely, the first 7 reference species B_1, B_2,…,B_7 are expected to be reactant compounds while the remaining reference species B_8, B_9,…,B_{17} are expected to be product compounds. In terms of the general reaction equation it means species B_1, B_2,…,B_7 should always have negative stoichiometric coefficients, i.e., be on the same side of the reaction as the test hydrocarbon **B**. From the above general reaction equation it follows that the WHSA partition of the species into reactant and product compounds can be easily violated. Indeed, species B_2, B_3 and B_7 are supposed to be reactant products, i.e., should have negative stoichiometric coefficients. In reality, their stoichiometric coefficients are positive and, hence, these species are always elemental products. As an example, we provide the following "old" RC5

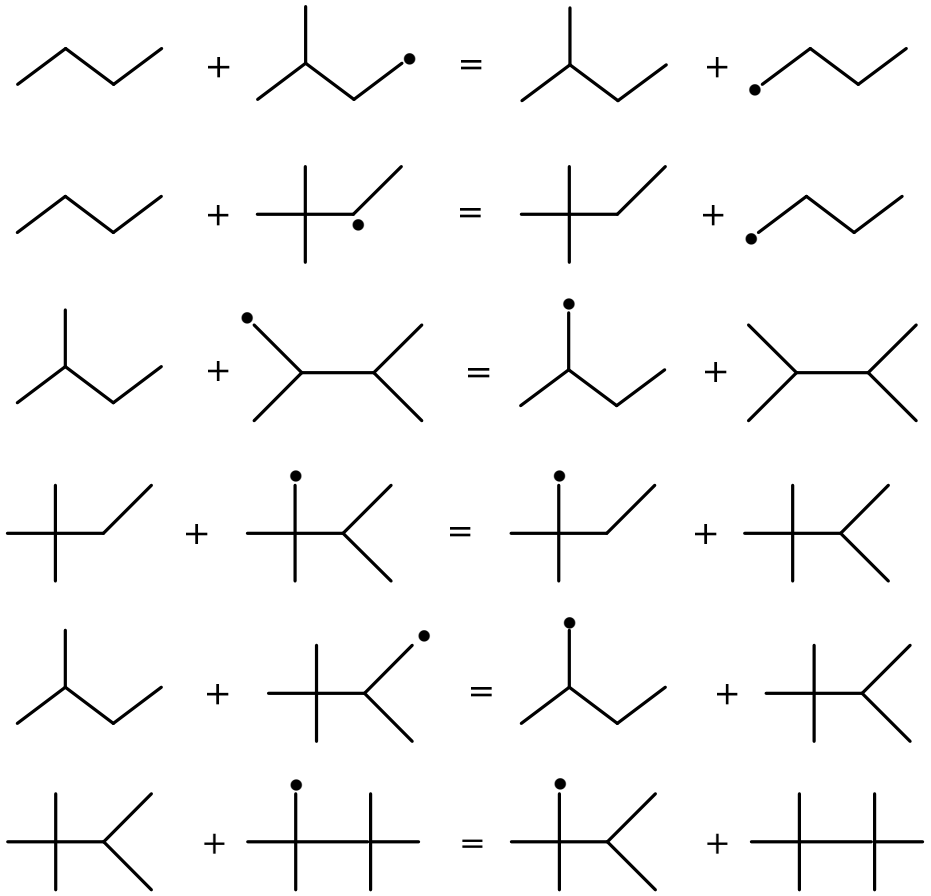


It is seen that in this reaction propylene (B_2) is a product compound and not a reactant compound as suggested by WHSA.

"New" Hyperhomodesmotic Reactions (RC5)

The "new" RC5 reactions are more problematic. According to WCW the "new" RC5 reactions should preserve the "numbers of carbon-carbon bond types inclusive of carbon hybridization and number of hydrogens attached". Incredibly, WCW did not even try to list or count the number of such bonds or groups. We, first, observe that the RC5 reactions essentially preserve the number and type of bonds as defined by Tatevski. [3] Indeed, according to Tatevski there are ten types of carbon-carbon bonds. Namely, six single C-C type of bonds, three double C=C type of bonds and one triple C≡C type of bond. These are presented in Scheme 3. Now, counting for possible number of hydrogen atoms connected to each carbon atom we arrive at a total of 38 groups that are presented in Table 3. A straightforward analysis of the groups matrix shows that its rank is equal to q = 34, i.e., equal to the number of species n = 34. Apparently, we are all set and the problem does have a unique solution, that is, the RC5 reactions are unique. Not so. A look at the group matrix reveals that the column corresponding to group g_{35} is empty, i.e., all entries are zero. This means that there is no way to generate a "new" RC5 reaction for a hydrocarbon that involves the group $C(sp^2)$ = C(sp). It is, therefore necessary, to introduce an additional reference species that involve this group, say, 1,1-dimethylallene. In Scheme 2 this species is labeled B_{35}. With this additional species the rank of the group matrix is equal to q = 35 and, hence, a unique "new" RC5 reaction for any conceivable hydrocarbon **B** may be always generated employing all 35 species in Scheme 2.

Of course, this type of reaction scheme can be expanded to hydrocarbon radicals too. However, if we wish to generate a unique reaction scheme that involves hydrocarbon radicals, it is necessary not only to clearly define the groups for radicals but carefully list and count them. We employed the formalism described above to analyze only the alkane radicals and easily found a violation of the principle of uniqueness. Thus, the following "new" RC5 reactions among reference species are valid



It means that six out of twenty one alkane radicals from the list presented by WCW can be dropped out. Alternatively, a "new" unique RC5 reaction can be generated employing only nine alkanes listed in Scheme 2 and fifteen alkane radicals. Again, the selection of the fifteen alkane radicals from a total of twenty one is not unique.

REFERENCES

(1) Wheeler, S. E.; Houk, K. N.; Schleyer, P. v. R.; Allen, W. D. *J. Am. Chem. Soc*. **2009**, *131*, 2547.

(2) Wodrich, M. D.; Corminboeuf,C.; Wheeler, S. E. *J. Phys. Chem. A* **2012**, *116*, 3436.

(3) Tatevskii, V. M. *The Structure of Molecules*; Khimiya: Leningrad, 1977.

Table 1. The Groups Defining the RC4 Reactions

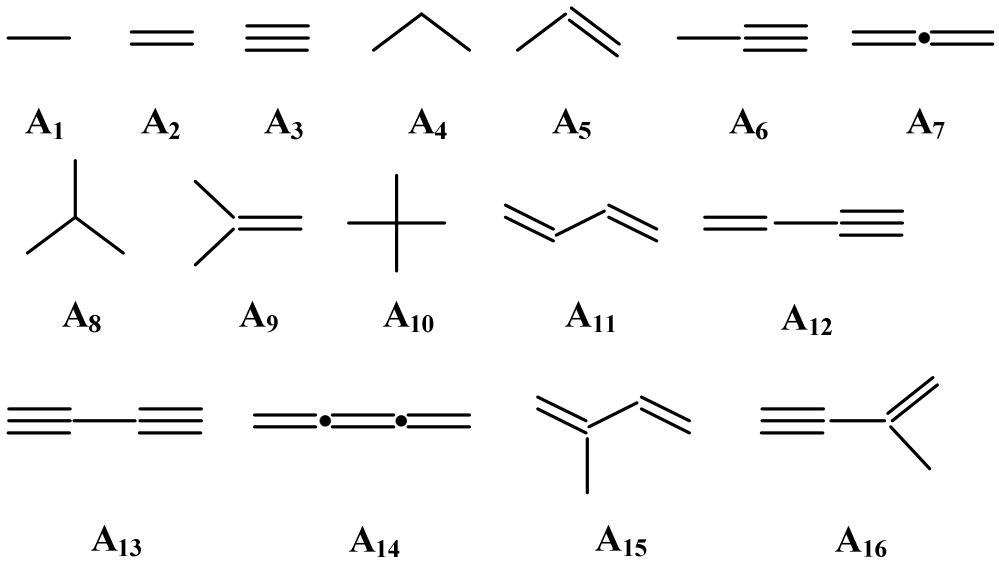
g_1:	$C(sp^3)$ - $C(sp^3)$	g_{11}:	$CH_3(sp^3)$
g_2:	$C(sp^3)$ - $C(sp^2)$	g_{12}:	$CH_2(sp^3)$
g_3:	$C(sp^3)$ - C(sp)	g_{13}:	$CH(sp^3)$
g_4:	$C(sp^2)$ - $C(sp^2)$	g_{14}:	$C(sp^3)$
g_5:	$C(sp^2)$ - C(sp)	g_{15}:	$CH_2(sp^2)$
g_6:	C(sp) - C(sp)	g_{16}:	$CH(sp^2)$
g_7:	$C(sp^2)$ = $C(sp^2)$	g_{17}	$C(sp^2)$
g_8:	$C(sp^2)$ = C(sp)	g_{18}:	C(sp) (=C=)
g_9:	C(sp) = C(sp)	g_{19}:	HC(sp)
g_{10}:	C(sp) ≡ C(sp)	g_{20}:	C(sp)

Table 2. The Groups Comprising the "old" RC5 Reactions

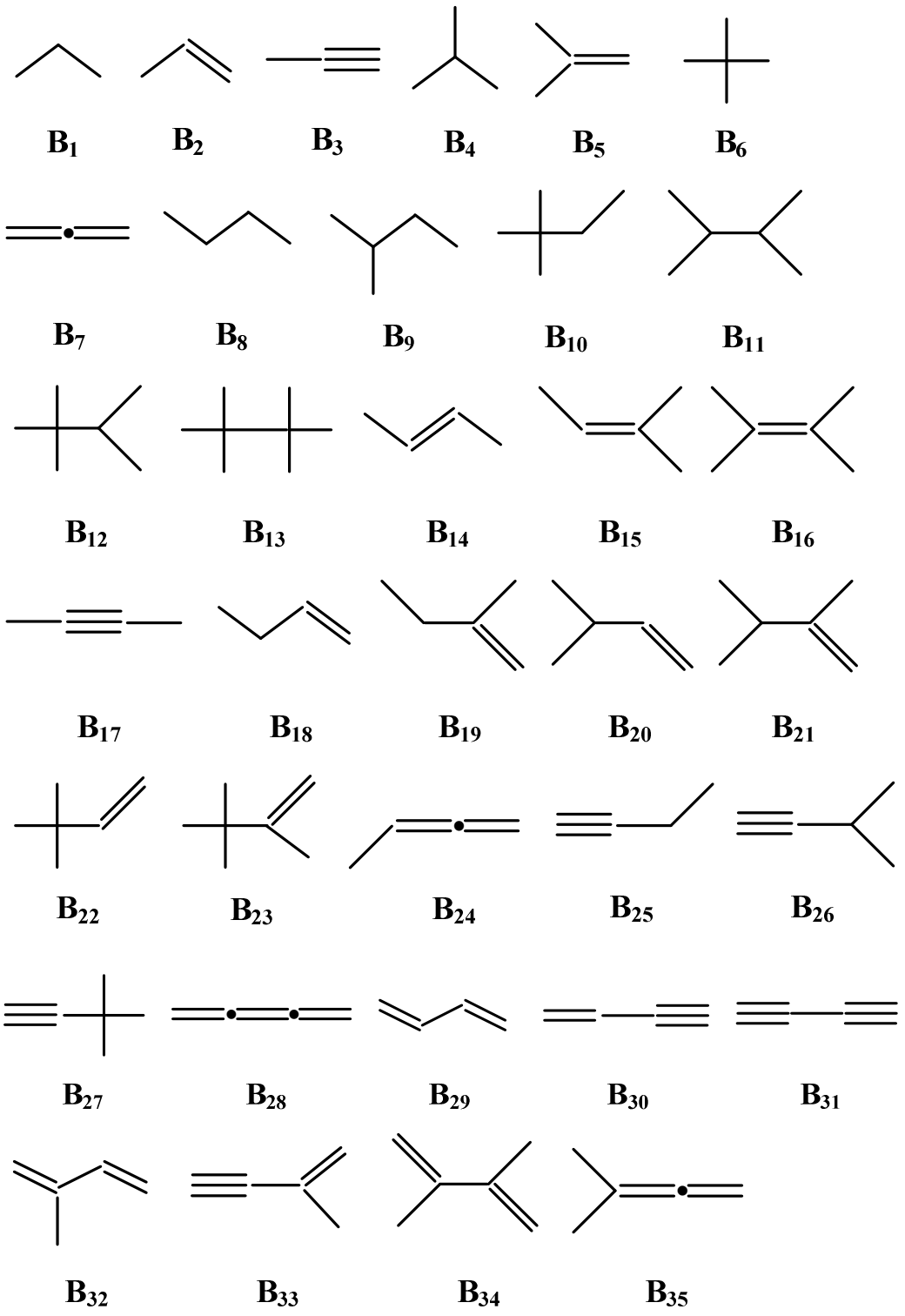
g_1:	CH_3-CH_2	g_{14}:	C=C
g_2:	CH_3-CH	g_{15}:	HC≡C
g_3:	CH_3-C	g_{16}:	C≡C
g_4:	CH_2-CH_2	g_{17}:	=C=
g_5:	CH_2-CH	g_{18}:	$CH_3(sp^3)$
g_6:	CH_2-C	g_{19}:	$CH_2(sp^3)$
g_7:	CH-CH	g_{20}:	$CH(sp^3)$
g_8:	CH-C	g_{21}:	$C(sp^3)$
g_9:	C-C	g_{22}:	$CH_2(sp^2)$
g_{10}:	CH_2=CH	g_{23}:	$CH(sp^2)$
g_{11}:	CH_2=C	g_{24}:	$C(sp^2)$
g_{12}:	CH=CH	g_{25}:	CH(sp)
g_{13}:	CH=C	g_{26}:	C(sp)

Table 3. The Groups Defining the "New" RC5 Reactions

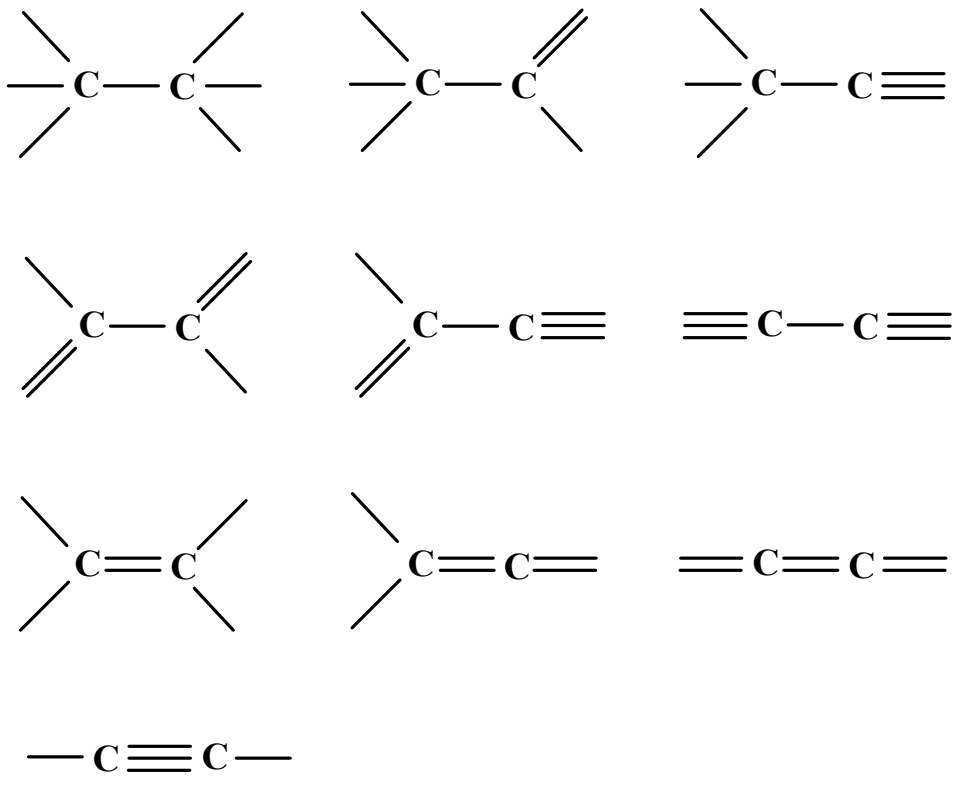
g_1:	$CH_3(sp^3)$ - $CH_2(sp^3)$	g_{20}:	$CH(sp^3)$ - $C(sp)$
g_2:	$CH_3(sp^3)$ - $CH(sp^3)$	g_{21}:	$C(sp^3)$ - $C(sp)$
g_3:	$CH_3(sp^3)$ - $C(sp^3)$	g_{22}:	$CH(sp^2)$ - $CH(sp^2)$
g_4:	$CH_2(sp^3)$ - $CH_2(sp^3)$	g_{23}:	$CH(sp^2)$ - $C(sp^2)$
g_5:	$CH_2(sp^3)$ - $CH(sp^3)$	g_{24}:	$C(sp^2)$ - $C(sp^2)$
g_6:	$CH_2(sp^3)$ - $C(sp^3)$	g_{25}:	$CH(sp^2)$ - $C(sp)$
g_7:	$CH(sp^3)$ - $CH(sp^3)$	g_{26}:	$C(sp^2)$ - $C(sp)$
g_8:	$CH(sp^3)$ - $C(sp^3)$	g_{27}:	$C(sp)$ - $C(sp)$
g_9:	$C(sp^3)$ - $C(sp^3)$	g_{28}:	$CH_2(sp^2)$ = $CH(sp^2)$
g_{10}:	$CH_3(sp^3)$ - $CH(sp^2)$	g_{29}:	$CH_2(sp^2)$ = $C(sp^2)$
g_{11}:	$CH_3(sp^3)$ - $C(sp^2)$	g_{30}:	$CH(sp^2)$ = $CH(sp^2)$
g_{12}:	$CH_3(sp^3)$ - $C(sp)$	g_{31}:	$CH(sp^2)$ = $C(sp^2)$
g_{13}:	$CH_2(sp^3)$ - $CH(sp^2)$	g_{32}:	$C(sp^2)$ = $C(sp^2)$
g_{14}:	$CH_2(sp^3)$ - $C(sp^2)$	g_{33}:	$CH_2(sp^2)$ = $C(sp)$
g_{15}:	$CH(sp^3)$ - $CH(sp^2)$	g_{34}:	$CH(sp^2)$ = $C(sp)$
g_{16}:	$CH(sp^3)$ - $C(sp^2)$	g_{35}:	$C(sp^2)$ = $C(sp)$
g_{17}:	$C(sp^3)$ - $CH(sp^2)$	g_{36}:	$C(sp)$ = $C(sp)$
g_{18}:	$C(sp^3)$ - $C(sp^2)$	g_{37}:	$CH(sp)$ ≡ $C(sp)$
g_{19}:	$CH_2(sp^3)$ - $C(sp)$	g_{38}:	$C(sp)$ ≡ $C(sp)$



Scheme 1. Hydrocarbons Used as Reference Species in RC4 Reactions



Scheme 2. Hydrocarbons Used as Reference Species in "Old" RC5 Reactions (First 34 Species) and "New" RC5



Scheme 3. Types of Carbon – Carbon Bonds Defined by Tatevski