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The thermodynamic imperative of the product specificity of chemical reactions and predicting *a priori* circumvention by catalysts

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Abstract

Catalysts promote the alteration of the product mix of chemical reactions (usually) from a greater to a lesser thermodynamic favorability. Catalyst identification requires that a significant number of empirical experiments be performed. There is, as yet, no method to conclusively identify specific catalysts for a particular reaction product mix *a priori*. However, if elementary reactions that make up the overall (most) thermodynamically favorable reaction can be interrogated, it is possible to identify those elementary reactions that produce the desired product mix. From a knowledge of the mechanism of these elementary reactions, it becomes possible to identify subsets of catalysts *a priori* that promote these mechanism(s). This paradigm requires more research to investigate catalytic mechanisms (rather than catalytic composition) so that *a priori* selection of catalysts from a knowledge of elementary reactions mechanisms becomes possible.

Given that multiple compounds can theoretically be formed from a combination of specific reactants, it becomes worthwhile to answer the following questions:

a. If multiple products can be formed, why is it that only certain products – and no others - are formed, under defined pressure, temperature and no limiting reactant (stoichiometric abundance) conditions?
b. Is there an *a priori* method or theory to predict which products are formed from given reactants, under defined pressure, temperature and no limiting reactant (stoichiometric abundance) conditions?
c. Lastly; can conditions of the reaction be changed by adding catalysts so that the reactions predominantly yield products that are more socially, environmentally and/or economically favorable? For example, can combustion reactions be made to predominantly produce CO and H_2 *via* reaction 4 and/or H_2 and CO_2 *via* reaction 14; instead of CO_2 and H_2O *via* reaction 1?

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As an illustrative example, the combination of acetylene and oxygen will be considered to answer the above questions. This combination was chosen because of the ability to form a multitude of different products as shown in the list below.The reactions below are identified as 'overall reactions' for the purpose of discussion in this paper. The enthalpy and entropy changes, ΔH_{rxn} and ΔS_{rxn}, for these individual overall reactions were calculated from the following equations respectively:

$$\Delta H_{rxn} = \sum (\text{bond breaking enthalpy})_{reactants} - \sum (\text{bond forming enthalpy})_{products}$$

$$\Delta S_{rxn} = \sum \Delta S_{products} - \sum \Delta S_{reactants}$$

1. $2\ C_2H_2 + 5\ O_2 \rightarrow 4\ CO_2 + 2\ H_2O$
2. $2\ C_2H_2 + O_2 \rightarrow 4\ C + 2\ H_2O$
3. $6\ C_2H_2 + O_2 \rightarrow 2\ C_6H_5OH$ (phenol)
4. $C_2H_2 + O_2 \rightarrow 2\ CO + H_2$
5. $C_2H_2 + O_2 \rightarrow C + H_2 + O_2$
6. $C_2H_2 + O_2 \rightarrow HCOOH + C$ (formic acid)
7. $C_2H_2 + O_2 \rightarrow HCHO + CO$ (formaldehyde)
8. $3\ C_2H_2 + 3\ O_2 \rightarrow C_6H_6O_6$ (Benzenehexol)
9. $C_2H_2 + O_2 \rightarrow C_2H_2O_2$ (acetylenediol, glyoxal)
10. $2\ C_2H_2 + 2\ O_2 \rightarrow C_4H_4O_4$ (fumaric acid, maleic acid)
11. $5\ C_2H_2 + 5\ O_2 \rightarrow C_{10}H_{10}O_{10}$ (cyclopentane pentacarboxylic acid)
12. $3\ C_2H_2 + 3\ O_2 \rightarrow C_6H_6O_6$ (aconitic acid)
13. $2C_2H_2 + O_2 \rightarrow CH_4 + CO_2 + 2C$ (methane)
14. $C_2H_2 + 2O_2 \rightarrow 2CO_2 + H_2$

The bond breaking enthalpies were obtained from reference 1. The ΔS values of the majority of the reactants and products were obtained from the computational chemistry comparison and benchmark database (2) calculated from the Density Functional Theory (DFT). The ΔS values of acetylene-diol and cis-aconitic acid were calculated by dividing the heat of fusion by the temperature in Kelvin at the melting point, which in turn were obtained from references 3 and 4 respectively. The ΔS values for the products of reactions 8 and 11 were not available in the literature. Hence, their ΔG_{rxn} could not be calculated. It was assumed that the values of ΔS and ΔH were temperature independent.

The free energy change for each overall reaction was calculated from the Gibbs-Helmholtz equation

$\Delta G = \Delta H - T\Delta S$, where T was taken as 298 K

Table 1: Calculation of enthalpy, entropy and free energy change for acetylene combustion reactions

Overall Reaction #	ΔH_{rxn} (kJ.mol^{-1})	ΔS_{rxn} (J.mol^{-1} K^{-1})	ΔG_{rxn} (kJ.mol^{-1})	Ln k (from elementary reactions), from Table 2
1	-1220	-177.8	-1167.3	13.05
2	987	-227.6	1052.8	11.34
3	786	-797	1023.5	
4	-420	120.8	-384.0	13.03
5	1229	-71.2	1242.2	11.99
6	127	-156.8	173.7	
7	-537	12.8	-540.8	12.89
8	-444	Not available	Not calculated	
9	-321	-358.9	-214.3	
10	-115	-647.7	77.8	
11	-156	Not available	Not calculated	
12	229	-806.5	11.2	
13	288	-205.2	349.1	11.9
14	-977	-46.2	-963.3	13.7

It can be seen from table 1 that reaction 1 is the most thermodynamically favorable of all the reactions, because it has the greatest negative free energy change. This is followed by reactions 14, 7 and 4, in that order. Chemiluminescence arising from OH*, CHO*, CH* and C2 * excited radicals measured during the course of the combustion reaction 1 indicated that the overall reaction involved multiple elementary steps. Kinetic modeling to reproduce the experimental Chemiluminescence indicated a reaction mechanism with 37 species and 106 elementary reactions (5). Products of reactions 2, 4, 5, 7, 13 and 14 appeared in those elementary reactions. The natural logarithm of the rate constants of the reactions (from reference 5) were calculated from all the reactions in which that specific product appeared regardless of whether or not that product was present as a reactant in a (previous or) subsequent reaction or whether the elementary reactions occurred in a sequential manner. The above two assumptions accounted for the wide variability in rate constants for a specific product, as is evident in the range for each value in table 2. The natural logarithm of the rate constants are tabulated in table 2. The rate constants (first order) were calculated using the equation

$$K = A.\ e^{-E/RT}$$

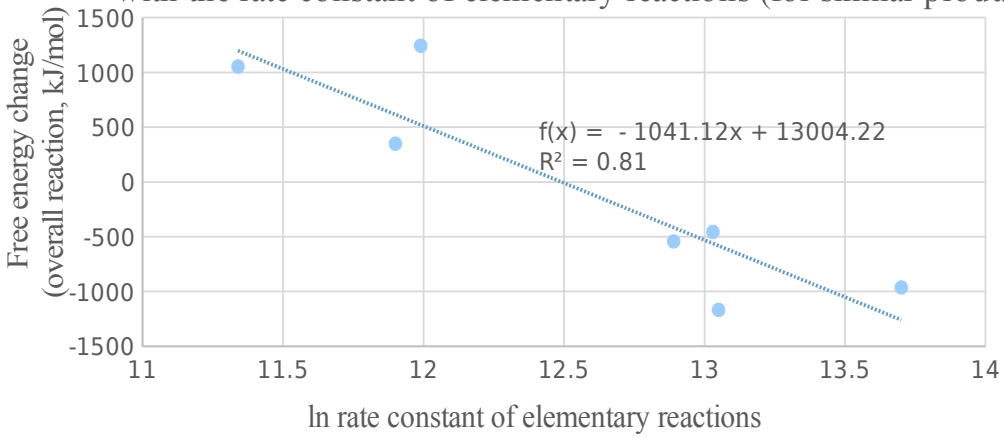
Where K=rate constant (s^{-1}), A = pre-exponential frequency factor (s^{-1}), E= activation energy ($J.mol^{-1}$), R = gas constant ($J.mol^{-1}\ K^{-1}$) and T = absolute temperature (K).

Table 2: average rate constants at 1350 K of elementary reactions for the combustion of acetylene (as calculated from reference 8)

Number of elementary reactions	Average Ln k (range)	Products of elementary reaction	Overall reaction No. for that product
8	12.84 (10.73-14.48)	HCHO	7
22	12.93 (10.59-14.28)	CO	4,7
16	13.12 (6.58-21.31)	H_2	4,5,14
1	10.58 (NA)	CH_4	13
9	14.27 (6.67-14.68)	CO_2	1,13,14
12	11.82 (7.09-14.00)	H_2O	1,2
2	10.85 (7.49-14.20)	C	2,5,6,13

The fact that there exists a negative correlation (Figure 1) between the rates of elementary reactions and the free energy change of the corresponding overall reactions (that produce similar products) indicates that the lower the activation energy of elementary reactions that result in specific overall reactions and products, the greater the (favorable) free energy change associated with that overall reaction. This is not entirely unexpected because the overall combustion reactions are irreversible and essentially proceed to completion.

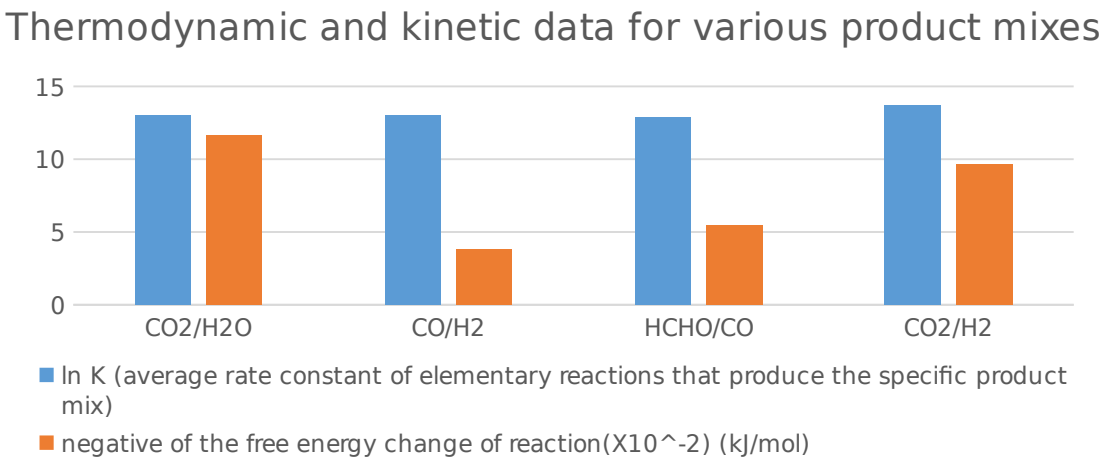
Figure 1: Correlation between the free energy change of overall reaction with the rate constant of elementary reactions (for similar products)



Therefore, for an irreversible reaction that can generate multiple products, the product mix can be altered by manipulating the activation energy associated with those elementary reactions that form the desired products. Since the mechanism of individual elementary reactions can be deduced from first principles, a catalyst that favors that specific mechanism can be identified a priori. Hence, instead of performing numerous empirical experiments encompassing the product-mix space, using design of experiments (DoE) protocols, reactions can be driven toward specified product mixes by catalytic – *mechanism based* - intervention of those elementary reactions that correspond to the generation of those desired and specified overall products. Furthermore, assuming that desirable products of the overall reaction are also those for which the activation energy of the corresponding elementary reactions is close to minimum, the predictability of successful catalytic intervention of these elementary reactions is increased.

To increase the efficiency with which a catalyst may alter the reaction pathway toward less thermodynamically favored products, the rate constants of the altered (elementary) reactions should be of the same order of magnitude as those for the thermodynamically favored (elementary) reaction. As a first approximation, this implies that the potential energy barrier for these two sets of reactions is similar when plotted on a potential energy *versus* reaction coordinate diagram. Furthermore, the ΔG of the 'less thermodynamically favored reactions' must be <0. From a comparison of tables 1 and 2, it can be seen that the rate constants of elementary reactions that generate the formation of products from overall reactions 4 and 14 are similar in the order of magnitude to the rate constant for the elementary reactions that form the products of elementary reaction 1.

Figure 2: Identifying overall reactions for greatest catalytic intervention efficiency



Furthermore, the ΔG_{rxn} for reactions 4 and 14 is <0; i.e. they are thermodynamically favorable. Hence, catalytic intervention to form either the products CO and H_2 (syngas) or the products CO_2 and H_2 would be the most likely to shift the product mix from CO_2 and H_2O (Figure 2).

From reference 5, out of the 16 elementary reactions that yield diatomic hydrogen as a product, 10 reactions use *in situ* generated monoatomic hydrogen as a reactant. This implies that the formation of H_2 is preferred when the C-H bonds of the starting hydrocarbon are broken, rather than when the C-C bonds are broken as is conventionally done *via* the process of cracking. Therefore, catalysts that favor C-H bond breaking over C-C bond breaking may produce H_2 via overall reactions 4 and/or 14. Such hydrogen-abstracting catalysts have been reported in the literature (6-8). In fact – as a validation of this approach – it turns out that the *in situ* conversion of gasoline to syngas by an onboard reformer is being actively pursued as a means to generate H_2 to more efficiently power automobiles (9, 10), using metal/metal oxide catalysts as hydrogen abstracting agents (11).

On the other hand, the catalyst must preferentially kinetically favor the desired elementary reaction pathway. In other words, it must be able to decrease the activation energy barrier of the reaction that produces the desired products – but not decrease the activation energy barriers of other elementary reactions that do not produce those products, regardless of thermodynamic favorability.

It is obvious that catalysts can also be employed for reaction pathways other than combustion, such as hydrogenation, carboxylation, polymerization etc. However, combustion is a *distributed* point-of-use pathway for burning fossil fuels, hence productive catalytic manipulation of this specific pathway has the potential to significantly reduce greenhouse gases and pollutants.

Conclusions

Under specific conditions of pressure, temperature and stoichiometric abundance, reactions produce those products for which there is a maximum overall decrease in free energy of the system. Therefore, from thermodynamic considerations alone, it is possible to predict, *ab initio*, the products that will form from known reactants assuming that a large enough combination and permutation set of products can be computed.

For combustion reactions which are irreversible and proceed to completion, the rate constants of elementary reactions are directly proportional to the thermodynamic favorability of the

overall reaction that forms the same products as those formed in the elementary reactions. This implies that catalytic intervention to decrease the activation energy of specific elementary reactions will shift the product mix of the overall reaction in the direction of the products that are formed by these elementary reactions. This conclusion is significant from a mechanistic point of view because it can link *catalytic mechanisms* – as opposed to *catalytic composition* - to desired product mixes from alternative thermodynamically favorable overall reactions; a paradigm that has not yet been proposed or evaluated.

Various possibilities and avenues of research arise from this work. In industrial, or distribute point-of-use combustion processes which can be interrogated for elementary reactions, it may be possible to predict which of those elementary reactions are more amenable to catalytic intervention – and by what catalytic mechanism - hence knowing which products are likely to form from such intervention (12). Catalysts that drive a specific overall desired reaction can be selected *a priori*, using a knowledge of the mechanism of the corresponding elementary reaction(s). This knowledge reduces the amount of experiments that need to be performed as part of a DoE protocol and significantly speeds up innovation and discovery – consider the fact that a suitable catalyst was found for the Haber-Bosch process only after performing 10000 experiments utilizing over 2000 catalysts (13). Even computational analysis of catalyst effectiveness can only provide agreement with empirical data; it cannot provide *a priori* selection (14).
More research to investigate catalytic mechanisms is needed so that the a priori selection of catalysts from a knowledge of elementary reaction mechanisms becomes possible.

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