

## KINETIC STABILITY OF UNSATURATED ORGANICS AT HIGH TEMPERATURES

Wing Tsang  
Chemical Kinetics and Thermodynamics Division  
National Institute of Standards and Technology  
Gaithersburg, Maryland 20899

### Introduction

Key words: unsaturated organics, kinetics, decomposition

Chemical processes involving organic compounds at high temperatures are controlled largely by the chemical and thermal stability of the unsaturated compounds that are formed during the decomposition process. This report reviews recent quantitative work dealing with these questions in the context of the thermal kinetics of reactions of such molecules in purely pyrolytic systems. It will also seek to highlight some of the important uncertainties in the understanding of the kinetics of such systems. The paper will begin with a summary of the present state of knowledge on the strength of the bonds (bond dissociation energies) that hold an unsaturated compound together. This will be followed by discussions on unimolecular reactions of molecules and radicals. For the former, bond dissociation and molecular processes will be considered. In the case of radicals, interest is on dissociation and isomerization. Bimolecular processes to be covered include metathesis and radical addition to stable compounds and radical combination with other radicals. Many of these processes are relatable to each other through the equilibrium constants. Thus the correct thermochemistry for reaction intermediates will be an underlying theme throughout this paper.

### Bond Energies

The addition of unsaturation to an alkane leads to drastic changes in the strength of the bonds in the molecule. The general situation in terms of a number of typical cases is summarized in Figure 1<sup>1-4</sup>. It can be seen that the bonds immediately adjacent to the site of unsaturation are strengthened, while those beta to that site are weakened. Thus the smallest unsaturates such as ethylene and acetylene, in terms of bond breaking through unimolecular decomposition, are rendered more stable. Indeed, for these compounds, unimolecular bond cleavage is probably not an important initiation reaction in comparison to radical induced decomposition processes under the conditions of most practical systems. For larger species, unsaturation leads to destabilization. This is a direct manifestation of the resonance energy of the new radicals that are formed.

There are still considerable uncertainties on the exact values of the bond energies given above. This may not be too serious for many high temperature applications, since the dependence on the activation energies decrease with temperature. It is however less satisfactory in cases where accurate branching ratios are required. As will be surmised from the subsequent discussion, there is now good capability for extrapolation and interpolation. Predictions can still be subject to large errors.

## Unimolecular Decomposition Processes

Table 1 contains rate expressions for bond breaking processes involving olefins<sup>2</sup>, aromatics<sup>4</sup>, alkynes<sup>2</sup> and a representative alkane<sup>2</sup>. All the reactions of the unsaturated compounds lead to the formation of resonance stabilized radicals and represent important dissociation channels. It can be seen that the differences in the activation energy from the alkane can be accounted quite accurately by the resonance energy. There is also a consistent decrease in the A-factor for the decomposition of the unsaturated compounds. It is possible to account for this by the more "tightened" structure of the resonance stabilized radical in comparison to that of the alkyl radicals formed during the decomposition of the alkanes. Of particular interest are the three dienes, 1,7-octadiene<sup>5</sup>, 1-7 octadiyne<sup>7</sup> and 1,5 hexadiene<sup>8,6</sup>. In the first case, the results are consistent with the assumption that substitution gamma to the bond being broken will have negligible effects. There is a factor of 2 divergence from this correlation for 1,6octdiyne. The data for 1,5 hexadiene are derived from the results on the allyl combination process. Although the A-factor appears to be slightly smaller than what would have been expected on the basis of the general trends, the discrepancies are not particularly large. Thus given the rate expression for an alkane it is quite straightforward to derive a similar expression for an unsaturated compound.

The resulting rate expressions leads to rate constants that are consistently larger than that for the comparable alkanes. This is especially true at the lower temperatures where the activation energies have larger effects on the rate constants. Unlike the alkanes, the larger unsaturated compounds can also decompose through a molecular "retro-ene" channel. This involves passage through a six centered transition state<sup>2</sup>. Some experimentally determined rate expressions can be found in Table 3.<sup>1</sup> Figure 2 contains Arrhenius plots for decomposition of 1-hexene and 1-hexyne through bond breaking and retro-ene channels. The larger rate constants for C-C bond cleavage in 1-hexene compared to that for 1-hexyne are entirely due to the change in the resonance energy of the two radicals formed during decomposition. However, the ordering is reversed for the molecular decomposition channel. From purely geometric considerations one would have thought that the preference would have been for 1-hexene since the 120° C-C-C bond angle in this compound should have resulted in less strain in the transition state than the linear C-C-C structure in 1-hexyne. The consequence is that the molecular process is more likely to be important for the decomposition of the latter. Interestingly, for the alkylbenzenes the retro-ene process appears to be much less important. At 1100 K it has not been possible to detect any contribution from this source in the decomposition of n-pentylbenzene<sup>4</sup>. In general, molecular channels becomes increasingly important with greater unsaturation. Thus, the predominant modes of 1,5 hexadiyne decomposition is to benzene and fulvene<sup>8,9</sup>.

Where there are no C-C bonds for which cleavage leads to resonance stabilized radicals, then the weakest bonds are the resonance destabilized C-H bonds. This however only moves these values to the upper end of the numbers for C-C bond cleavage in alkanes. Furthermore, the A-factor for C-H bond break can be expected to be somewhat smaller than that for C-C bond cleavage. An interesting situation arises for compounds such as propene and toluene where there the breaking of the C-C bond next to the site of

unsaturation may become competitive with that for C-H bond cleavage. In the case of toluene the experimental data are controversial<sup>10-11</sup>. The situation is made more uncertain by the fact that at the high temperatures required for these decompositions, the reactions are into the pressure dependent region. Thus it is not only necessary to have accurate high pressure rate expressions but also the energy exchange parameter. A satisfactory fit of the data pertaining to propene decomposition have been published recently<sup>12</sup>.

The stability of the small unsaturated compounds also brings into play the possibility of other modes of decomposition. Thus in the case of ethylene<sup>13</sup>, there is considerable evidence for a reaction channel involving vinylidene. For butadiene decomposition the data is suggestive of an analogous process<sup>14</sup>. In the case of cis-butene-2 the decomposition data have been interpreted in terms of the direct formation of butadiene<sup>15</sup>. In the case of benzene however, C-H bond cleavage appears to be the predominant decomposition mode under all conditions<sup>16</sup>. Another initiation process that is unique to unsaturated compounds is the possibility of radical formation through bimolecular reaction or the reverse of radical disproportionation reactions<sup>17</sup>. Rate expressions for these processes can be readily derived through the equilibrium constant and well established rate constants for the latter on the assumption that the temperature dependence of the disproportionation process is small.

There are very little data on the kinetics of the decomposition of unsaturated radicals. For the vinyl radical, one can calculate a high pressure rate expression on the basis of the reverse reaction and the thermodynamics<sup>13</sup>. However, under practically all high temperature conditions the process is well into the fall-off region. Thus it is necessary to determine a collision efficiency. Unfortunately, the lower temperature measurements on the pressure dependence cannot be fitted within the framework of RRRM theory. This leaves predictions of high temperature behavior very uncertain. The situation with respect to phenyl and benzyl radical is not completely clear<sup>18</sup>. They may be so stable that in most systems decomposition may not be an important destruction channel. This is probably the case for propargyl. The rate expression for the decomposition of allyl radical to form allene and hydrogen atom<sup>5</sup> have recently been determined. The rate expression consistent with the low temperature rates for the reverse reaction is  $5 \times 10^{13} \exp(-29500/T) \text{ s}^{-1}$ . This can be compared with a rate expression of  $4 \times 10^{13} \exp(-19000/T) \text{ s}^{-1}$ <sup>19</sup> for the comparable decomposition of isopropyl radical. There is thus over 20 kcal/mol difference in activation energy and is in fact much larger than the difference in that for C-H bonds in ethylene and ethane. On a per hydrogen basis the A-factor is somewhat larger and is consistent with the "stiffer" allyl as compared to alkyl radicals. In the case of butenyl-2, from the reaction of hydrogen with butadiene it is possible to derive the rate expression  $4 \times 10^{13} \exp(-24200/T) \text{ s}^{-1}$ . It would appear that the resonance energy is almost fully expressed in the activation energy of the decomposing species. Butenyl-3 contains a beta C-C bond that is adjacent to the double bond and a beta C-H bond that is also allylic. For alkyl radicals beta C-C bond cleavage is always the preferred decomposition mode. There is need for data on this and related unsaturated systems such as a butadienyl. The branching ratio for C-C and C-H bond cleavage have important consequences on models for the building of the larger unsaturated structures during hydrocarbon decomposition.

Larger alkyl radicals can readily isomerize through hydrogen migration. Transfer between the 1,4 and 1,5 appear to be more facile than the 1,2 and 1,3 reactions. At 1100 K contributions from the latter have been noted. Similar processes can occur for the unsaturated counterparts. In addition the latter can also cyclize. Thus 4-pentenyl-1 can cyclize to form the cyclopentyl radical<sup>5</sup>. There are large uncertainties in the rate expressions for such processes. Activation energies are expected to be low or in the 20 kcal/mol range and A-factor should reflect a "tight" transition state. This leads to major uncertainties in the nature of the breakdown products of the larger unsaturated molecules and is an important barrier in tracing the breakdown pathways of hydrocarbons in high temperature systems.

For high temperature unimolecular processes, it is necessary to consider at all times the effect of fall-off. In general, existing data can be fitted within the framework of RRKM calculations. The problem with vinyl mentioned earlier is probably the only exception. The requirements for making correct predictions are accurate high pressure rate expressions and the average energy transferred per collision and is particularly important for the estimation of branching ratios. This has been discussed earlier for propene decomposition. Low activation energy decomposition processes may have additional complications at high temperatures since a steady state distribution may not be achieved. Thus the standard treatment is not adequate and the solution of non-steady state master equation is required. Programs to carry out such calculations are now beginning to appear. It would be interesting to test such procedures with careful experiments.

#### Radical Attack

The weakness of the allylic and benzylic C-H bonds leads naturally to the assumption that rate constants for abstraction processes resulting in the formation of resonance stabilized species will be vastly enhanced over that for alkyl radicals. This is not the case and is demonstrated in Figures 2 and 3 where the comparison is for the abstraction of benzylic and allylic hydrogens by hydrogen and methyl and the corresponding alkane, propane. It will be noted that the 10-11 kcal/mol difference in the bond being broken if directly manifested in the activation energy would have led to differences of 2 orders of magnitude at 1100 K and 4 orders of magnitude at 550 K. Instead, in the case of abstraction by methyl it is apparent that the rate constants on a per hydrogen basis are commensurate with that from an secondary hydrogen. For abstraction by hydrogen atoms, rate constants on a per hydrogen basis are only a factor of 2 larger than that for the normal hydrogens and not even as large as that for a secondary hydrogen. It will be recalled that the difference in bond energies between primary and secondary hydrogens in alkanes is about 2 kcal/mol. These results are consistent with a transition state that is similar to the reactants and contrasts with the situation for unimolecular decomposition where the resonance energy is fully manifested. Consistent with the former is the relative constancy in the rate constant for the abstraction of benzylic and allylic hydrogens. These observations also can serve as a basis for prediction of abstraction rate constants for other reactions that lead to resonance stabilized products.

Through detailed balance one can then calculate the rate constant for

abstraction by resonance stabilized species. Due to the resonance destabilization of the bond this is an endothermic process. Since this is not made up by a faster abstraction rate constant in the forward direction, abstraction by resonance stabilized radicals must be quite slow. The consequence is that such species can cause chain termination through combination with other radical processes present in the system.

In the case of a vinylic C-H bond, the increase in bond strength appears to be manifested in the form of a smaller rate constant for the abstraction process. This can be seen in Figure 3, where the recent data for methyl abstraction<sup>20</sup> of a vinylic hydrogen from ethylene can be compared with the molecules discussed earlier. There are virtually no other reliable data on the rate constants of abstraction by vinylic or phenyl radicals. Since such processes are all more exothermic than comparable processes by methyl, it is very tempting to use the results from methyl as a lower limit.

Radicals can add to a site of unsaturation. In many instances this is a reaction that has no effect. For example terminal addition of H-atom to propene will lead to the formation of isopropyl radical which will readily go back to propene in high temperature systems. Terminal addition is the observed addition mode at room temperature. It has recently been found that the preference for terminal addition is mainly an enthalpic effect and is related to the stability of the radical that is formed<sup>21</sup>. Thus as the temperature is increased non-terminal addition becomes increasingly important. Non-terminal addition by hydrogen to a compound such as propene will lead to the formation of n-propyl radical which will decompose to form propene and methyl. The effect is that of a displacement reaction. Should the general trend hold then terminal addition to butadiene will be overwhelmingly favored and the induced decomposition by hydrogen atom to form vinyl and ethylene cannot be an important process. Addition processes, even at the non-terminal position have lower activation energies than the competitive abstraction processes. The A-factors are however lower. It is thus important at lower temperatures. Figure 4 summarizes data on hydrogen attack on isobutene and toluene<sup>22-23</sup>. It is clear that hydrogen addition to the olefin is favored over that for the aromatic. The overall effect of these processes is to remove the side chains from the unsaturated structure.

Resonance stabilization renders organic radicals much less thermally and chemically reactive. Thus it is expected that their steady state concentrations will be much larger. Reaction with itself and other organic radicals will then become important. The rate constants for such process are not much different than that of the non-resonance stabilized species. These radicals will also add to unsaturated compounds. As the temperature is increased the reaction will be reversed. The newly formed radical can also isomerize or cyclize. As a result one has a chemical activation system involving low activation energy process. There has been considerable recent work involving vinyl and phenyl addition to unsaturates<sup>24</sup>. As in the case for the resonance stabilized case these may be reversible. Alternatively the addition may be followed by ejection of a fragment of the original molecule. The results must then be treated in terms of a chemical activation process. Such treatment is handicapped by the fact that the experimental results are really a combination of several elementary single step processes. Without the rate expressions for the true elementary steps extrapolations and predictions may be unreliable.

### References

1. MacMillen, D. F. and Golden, D. M., *Annu. Rev. Phys. Chem.*, 33, 439, 1982
2. Tsang, W., "Comparative Rate Single Pulse Shock Tube in the Thermal Stability of Polyatomic Molecules," *Shock Tubes in Chemistry*, A. Lifshitz ed., Marcel Dekker, pg. 59, 1981.
3. Tsang, W., *J. Am. Chem. Soc.*, 107, 2873, 1985
4. Tsang, W., *J. Phys. Chem.*, 94, 3324, 1990
5. Tsang, W. and Walker, J. A., *J. Phys. Chem.* submitted
6. Tsang, W. and Walker, J. A.; "The Thermal Decomposition of Octadiyne as a Source of Propargyl Radicals" in preparation
7. Tulloch, J. M., Macpherson, M. T., Morgan, C. A. and Pilling, M. J., *J. Phys. Chem.*, 86, 3812, 1982
8. Stein, S. E., Walker, J. A., Suryan, M. M. and Fahr, A., 24th Sym. (Int.) on Combustion, (The Combustion Institute, Pittsburgh, Pa.), 1990, 85
9. Brown, R. F. C., *Pyrolytic Methods in Organic Chemistry*", Academic Press pg. 324
10. Pamidimukkala, E. M., Kern, R. D., Patel, M. R., Wei, H. C., and Kiefer, J. H., *J. Phys. Chem.*, 91, 2148, 1987
11. Muller-Markgraf, W. and Troe, J., 21st Symp. on Comb., 1988, 815
12. Tsang, W., *J. Phys. Chem. Ref. Data*, 20, 221, 1991
13. Tsang, W. *J. Phys. Chem. Ref. Data*, 15, 1087, 1986
14. Tsang, W. and C. Y. Lin, in preparation
15. Alfassi, Z. B., Golden, D. M., Benson, S. W., *Int. J. Chem. Kin.*, 5, 991, 1973
16. Hsu, D. S. Y., Lin, C. Y., Lin, M. C., 21st Symp. (Int.) on Comb. (The Combustion Institute, Pittsburgh, 1984, pg 623
17. Stein, S. E., "Free Radicals in Coal Conversion" in "Chemistry of Coal Conversion" (Schlosberg, R., ed.) Plenum Publishing, 1985, pg. 13
18. Kern, R. D., Wu, C. H., Skinner, G. S., Rao, V. S., Kiefer, J. H., Towers, J. A., and Mizerka, L. J., 20th Symp. (Int.) on Comb. (The Combustion Institute, Pittsburgh, Pa.) 1984 pg 789
19. Tsang, W. *J. Phys. Chem. Ref. Data.*, 17, 887, 1988
20. Zhang, H. X., and Back, M. H.; *Int. J. Chem. Kin.*, 22, 21, 35
21. Slagle, I. R., Batt, L., Gmurczyk, G. W., Gutman, D. and Tsang, W., *J. Phys. Chem.*, 95, 7732, 1991
22. Fahr, A. and Stein, S. E., *J. Phys. Chem.*, 92, 4951, 1988
23. Tsang, W. and Walker, J. A., 22nd Symp. (Int.) on Comb. (The Combustion Institute, Pittsburgh, Pa.), 1988, 101
24. Robaugh, D. and Tsang, W., *J. Phys. Chem.* 90, 4159, 1986.

Table 1: Rate expressions for various bond breaking processes(1100K).

$k(\text{hexane} \rightarrow 2\text{propyl}) \rightarrow 2.5 \times 10^{16} \exp(-41000/T) \text{ s}^{-1}$   
 $k(\text{hexene-1} \rightarrow \text{allyl} + \text{propyl}) \rightarrow 8 \times 10^{15} \exp(-35600/T) \text{ s}^{-1}$   
 $k(\text{hexyne-1} \rightarrow \text{propargyl} + \text{npropyl}) \rightarrow 8 \times 10^{15} \exp(-36300/T) \text{ s}^{-1}$   
 $k(1,7\text{octadiene} \rightarrow 4\text{-pentenyl} + \text{allyl}) = 1.2 \times 10^{16} \exp(-35700/T) \text{ s}^{-1}$   
 $k(1,7\text{octadiene} \rightarrow 4\text{-pentylnyl} + \text{propargyl}) = 1.6 \times 10^{16} \exp(-35760/T) \text{ s}^{-1}$   
 $k(1,5\text{hexadiene} \rightarrow 2 \text{ allyl}) = 7 \times 10^{14} \exp(-29500/T) \text{ s}^{-1}$   
 $k(\text{n-phenylbenzene} \rightarrow \text{benzyl} + \text{nbutyl}) = 1 \times 10^{16} \exp(-36500/T) \text{ s}^{-1}$   
 $k(1\text{-phenyl-1-pentene} \rightarrow 3\text{-phenyl-2-propenyl} + \text{ethyl}) = 3 \times 10^{15} \exp(-33800/T) \text{ s}^{-1}$

Table 2. Rate expressions for the decomposition of unsaturated compounds into molecular entities

$$\begin{aligned}
 k(\text{hexene-1} \rightarrow 2\text{propene}) &= 4 \times 10^{12} \exp(-28900/T) \text{ s}^{-1} \\
 k(1,7\text{-octadiene} \rightarrow 1,4, \text{pentadiene} + \text{propene}) &= 3 \times 10^{12} \exp(-27900/T) \text{ s}^{-1} \\
 k(1\text{-hexyne} \rightarrow \text{allene} + \text{propene}) &= 5 \times 10^{12} \exp(-28400/T) \text{ s}^{-1} \\
 k(6\text{-methylheptyne-2} \rightarrow 1,2\text{butadiene} + \text{isobutene}) &= 2 \times 10^{12} \exp(-28700/T) \text{ s}^{-1} \\
 k(1,7\text{octadiyne} \rightarrow \text{allene} + \text{pent-1-ene-4-yne}) &= 5.6 \times 10^{12} \exp(-27860/T) \text{ s}^{-1}
 \end{aligned}$$

Figure 1. Typical Bond Dissociation Energies for alkanes, alkylbenzenes, alkenes and alkynes.

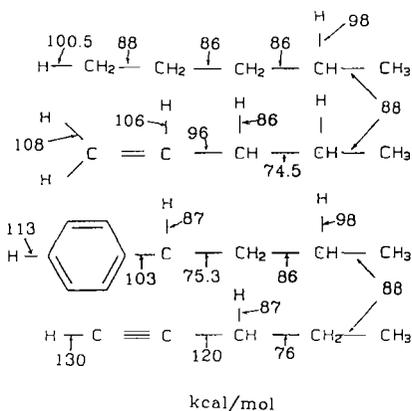


Figure 2. Rate constants for 1-hexene and 1-hexyne decomposition through bond breaking and retro-ene reactions.

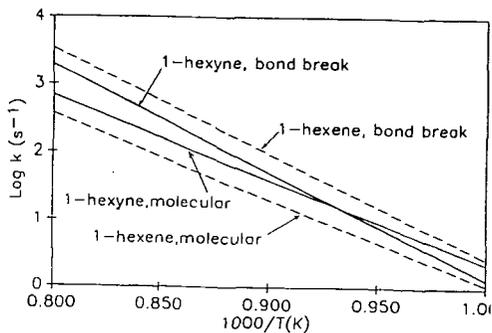


Figure 3. Rate constants for abstraction of hydrogen by hydrogen leading to benzyl, allyl, n-propyl and isopropyl radicals. [per hydrogen basis]

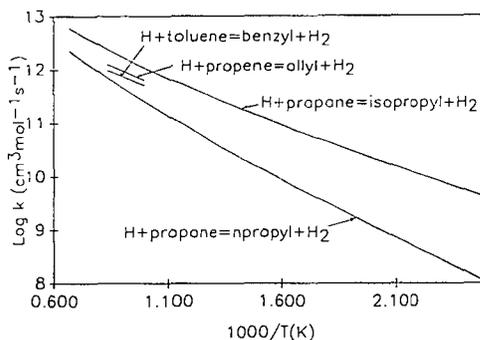


Figure 4. Rate constants for abstraction of hydrogen by methyl leading to benzyl, allyl, vinyl, isopropyl and n-propyl radicals. [per hydrogen basis]

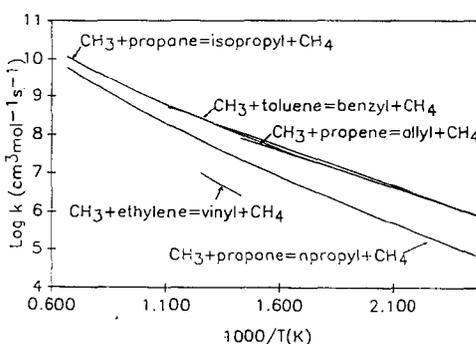


Figure 5. Rate constants for hydrogen atom attack on isobutene and toluene.

