

ANALYSIS OF CHEMICALLY-ACTIVATED PATHWAYS FOR MOLECULAR WEIGHT GROWTH

Anthony M. Dean
Exxon Research and Engineering Company
P. O. Box 998, Annandale, NJ 08801

and
Joseph W. Bozzelli
Department of Chemical Engineering and Chemistry
NJIT, Newark, NJ 07039

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The unusually rapid rate of molecular weight growth in high temperature pyrolysis and oxidation of hydrocarbons has presented a substantial challenge to kineticists. Although there has been progress recently in characterization of the rapid rate of growth, attempts to accurately model the process have been only partially successful. For example, the extensive study of Frenklach et al¹ required rate constants for radical addition reactions which are several orders of magnitude larger than usually observed for these types of reactions.

There appear to be three possible pathways to rapid molecular growth:

- (1) Diels-Alder cycloadditions reactions
- (2) Ion-molecule reactions with their very large rate constants
- (3) Radical addition to unsaturates

A major difficulty with (1) is that the equilibrium constants for this type of reaction suggest that the cyclic product would tend to dissociate to the linear fragments at high temperatures where the fast growth is observed. Ionic mechanisms are suspect since rapid growth is observed under pyrolytic conditions where the ion concentration would be expected to be extremely low. By default, then, our attention (like Frenklach et al) have focussed upon radical addition reactions. Previously, we demonstrated² that new reaction channels could open up at higher temperatures in chemically-activated reactions like those involving radical addition to unsaturates.

The methane pyrolysis data of Back and Back³ provided an opportunity to see if properly accounting for chemical activation might explain the observed sharp increase in rate of reaction at very low extents of conversion at temperatures near 1000K. It was possible to explain the observed acceleration⁴ and to demonstrate that a critical feature of the mechanism was the very rapid production of cyclopentadiene via chemically-activated pathways. These chemically-activated adducts have enough internal energy to react unimolecularly before collisional stabilization can occur; this significantly increases the overall rate of production of heavier species because no time is required for collisional deactivation and subsequent activation to get to the same products.

This analysis also led to some useful generalizations about features of potential energy surfaces which can lead to rapid growth. Specifically, it was found that allyl addition to acetylene was critical, while the analogous addition to ethylene was not

important, even though ethylene was present in much larger concentrations. Fig. 1 compares the potential surfaces for these two reactions. Note the differences in the energetics. First the well for acetylene addition is deeper by 8 kcal/mole. Furthermore, the difference in energy between the linear and cyclic intermediates is greater in the acetylene case by about 9 kcal/mole. Much of this difference can be attributed to the relatively high energy vinyllic radical ($C=CCC=C\cdot$). Even with respect to final products, the acetylene is overall exothermic while ethylene is endothermic. Each of these differences contribute to the enhancement for the acetylene reaction. The shallower well for ethylene addition will contribute to more stabilization since the barrier to cyclization is comparable to the entrance channel, while for acetylene the cyclization barrier is 11 kcal/mole lower. Similarly, the difference in energy between linear and cyclic intermediates means that the equilibrium constant for the cyclization involving $C=CCC=C\cdot$ is more favorable, i. e., by a factor of 60 at 1038K (the temperature of the Back and Back experiments), than for the cyclization of $C=CCCC\cdot$. Thus we expect cyclization, whether it occurs via stabilized or energized adducts, to be much more favored for the case of $C=CCC=C\cdot$; under the present conditions, this difference is enough to make contributions from allyl addition to ethylene unimportant. In general, the shallower wells in the ethylene system, coupled with the greater entropy of the reactants relative to the intermediates, favor redissociation of the adducts back to reactants, thus making this an inefficient channel for molecular weight growth.

These observations can be generalized to other addition reactions. The following factors should increase the probability that direct production of cyclic species can occur via an energized-complex mechanism:

- (1) A deep well for the linear adduct—this will tend to make the barrier to cyclization lower than the entrance barrier, thus increasing its unimolecular rate.
- (2) An increase in the exothermicity of the cyclization reaction—this is needed to offset the entropy loss upon cyclization.
- (3) A final cyclic product with high stability—this will result in low energy exit channels relative to the entrance and will lead to faster unimolecular rates.

One such system where these factors are especially significant is the formation of benzene via the sequence:



The potential energy diagram is shown in Fig. 2. Here the linear adduct is seen to give a much deeper well than that resulting from the allylic addition shown in Fig. 1. Here the adding radical is vinyllic, as contrasted to the resonantly stabilized allyl; thus there is no loss of resonance upon addition as is the case with allylic species. The cyclization is also much more favored in the benzene system since the combination of an unstable vinyllic linear radical and a very stable cyclic radical results in an exothermicity of 43 kcal/mole for the cyclization. Furthermore, note that the final exit channel for benzene production, due to its unusual stability as an aromatic molecule, is much lower than the entrance channel. As a result, this path to benzene can be very important. In fact, at 1 atm and 1200K, the rate of production of benzene via the direct reaction of the energized complex accounts for over 90% of the total reaction of the initially formed linear adduct. Here the overall exothermicity is sufficient to

compensate for the loss in entropy upon cyclization. Such compensation is particularly important at high temperatures where the $T\Delta S$ term plays a larger role.

Another interesting issue in molecular weight growth is the possibility of isomerization of methyl-cyclic C_5 compounds to cyclic C_6 compounds. Such isomerizations were considered in chlorobenzene pyrolysis to explain observed production of minor amounts of cyclopentadiene⁵. Given the prediction of cyclopentadiene production in methane pyrolysis, Fig. 3 suggests a possible route to benzene from cyclopentadiene. The recombination of the cyclopentadienyl radical with methyl is quite likely in these systems since both species are likely to build up to quite high concentrations, relative to other radicals, since there are no facile dissociation channels available. Note the production of methyl-cyclopentadienyl is only 8 kcal/mole endothermic. Once formed it can undergo beta-scission to form fulvalene. H-atom addition to the fulvalene (to the opposite end of the double bond) leads to the cyclopentadienylmethyl radical, which would be expected to quickly convert, over a series of low barriers, to benzene. This analysis would suggest that one really needs to consider formation of both 5 and 6 membered rings as the starting points for aromatics formation.

In an effort to better understand the detailed kinetics of molecular weight growth, we have used a molecular-beam sampling mass spectrometer (MBMS) to directly observe reactants, products, and reactive intermediates in hydrocarbon pyrolysis and oxidation⁶. A key component of this approach is use of photoionization at 10.5 eV, obtained by tripling the tripled (355 nm) output of a YAG laser. It is then possible to minimize fragmentation, substantially improving one's ability to observe free radicals that would otherwise be obscured by parent fragments. A schematic of the experimental set-up along with typical data from 1-butene pyrolysis is shown in Fig. 4. This system has been used to observe the production of both C_5 and C_6 species during pyrolysis and oxidation of C_4 molecules. In a typical experiment, the temperature is slowly increased at constant residence time and the molecular weight growth is monitored as one goes to higher conversions. A particularly interesting observation was that the allyl radical concentration was observed to decline at temperatures where C_5 and C_6 molecules were initially observed to be produced. We are now comparing these results with our detailed models of molecular weight growth.

An analysis of benzene production in low pressure flames⁷ led to the identification of several radical addition reactions that might account for the observed production. One such path was that considered above in (A). This path was chosen by comparison of the measured concentrations C_4H_5 and C_2H_2 to the rate of benzene production. However, since C_4H_5 was measured with a mass spectrometer, it was not possible to distinguish 1- C_4H_5 from 2- C_4H_5 . If these two isomers were equilibrated and if the secondary radical were much more stable, one would expect the majority of the measured C_4H_5 to be the secondary radical, which is not expected to rapidly form benzene, and this particular route would be unimportant. [However, it is important to note that the secondary radical can add to acetylene to form a fulvalene radical, and thus it might be converted to benzene in a second step, as discussed above.] Thus a critical issue, as yet not completely resolved, is the relative stability of these two isomers. At first glance, it might appear that the secondary radical would be much more stable, since the unpaired electron could be stabilized by the adjacent double bond. Indeed, The Sandia Thermodynamic database⁸ indicates a normal resonance

stabilization (12 kcal/mole) in the secondary radical. However, the rotation required here would disrupt the conjugation in the system as well as result in the relatively high energy allenic structure (1,2 butadiene is 12.5 kcal/mole less stable than 1,3 butadiene⁹). Thus, it might appear that the normal resonance stabilization could be offset, and the energies of two isomers could be quite close. We feel this is an area which warrants further investigation. For the flame work considered here, benzene production occurs near 1500K. This implies that a difference in stability of 3 kcal/mole in the two isomeric forms would result in 42% of the C₄H₅ as the primary isomer, meaning that this could be a major route to benzene. However, a difference of 12 kcal/mole, i. e., a typical resonance stabilization energy, would mean that only 4% of the primary isomer would be present at equilibrium; thus ruling out this direct path to benzene in this flame.

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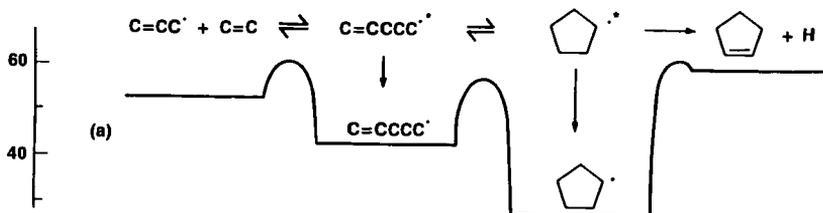
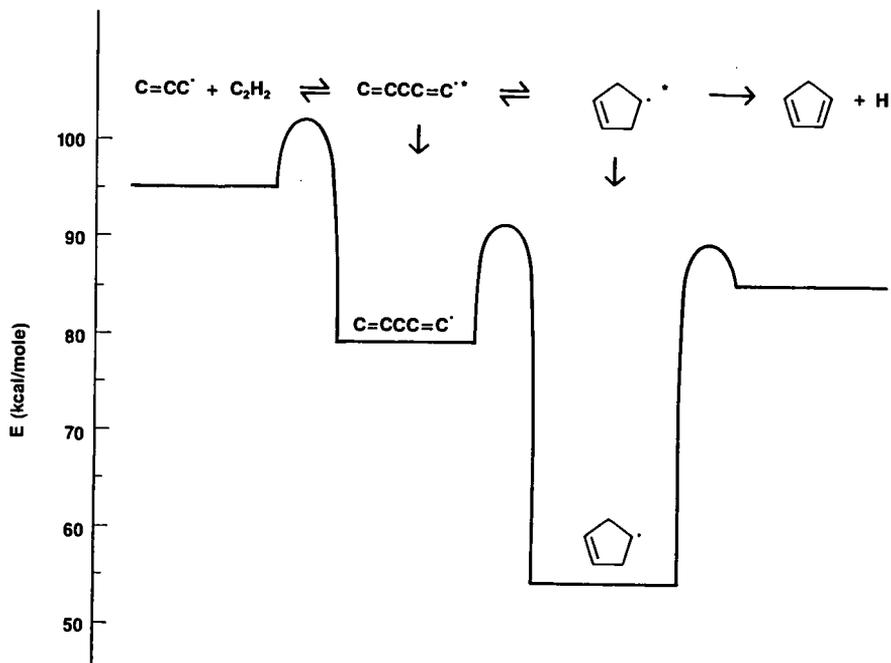
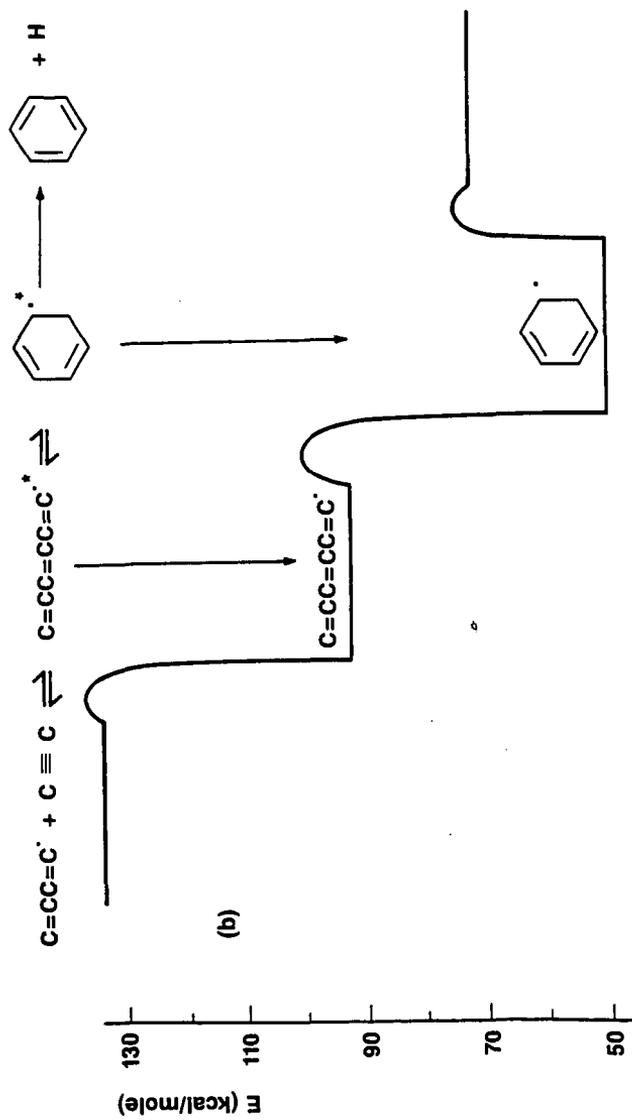


Figure 1

Figure 2



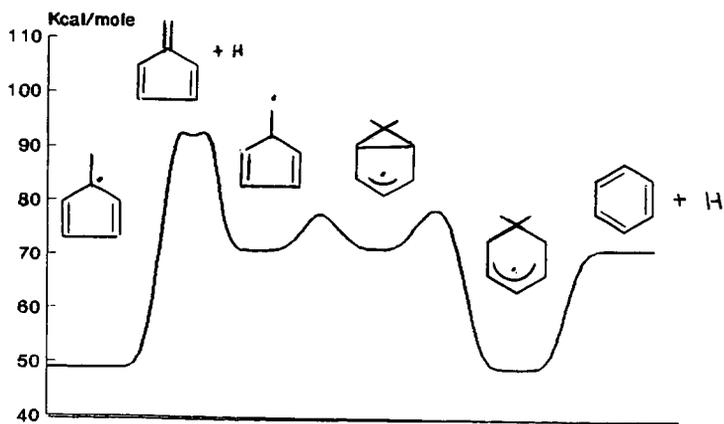
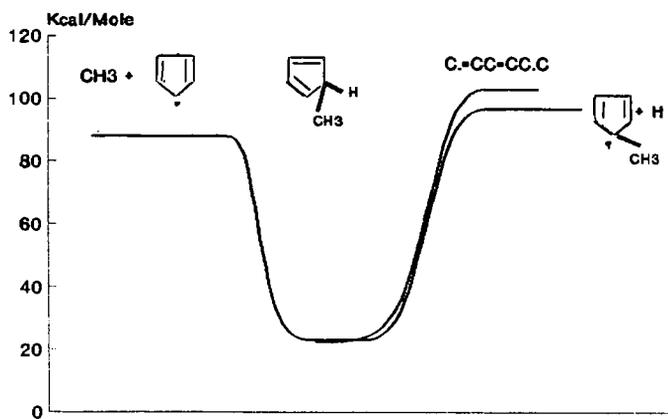


Figure 3

Figure 4

