Methyl Radical and Shift Reactions with Aliphatic and Aromatic Hydrocarbons: Thermochemical Properties, Reaction Paths and Kinetic Parameters

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Introduction

The study of soot formation under moderate to low (ca. 1100K), temperatures and pyrolytic conditions, no oxygen, with small hydrocarbons like acetylene, ethylene, methane, propane or propene in flow reactors is of interest for nanotube formation, and for many solid carbon products such as brake pads and carbon black, … etc. A fundamental understanding of soot formation chemistry is important to reducing soot emissions from vehicles and other combustion sources.

Our attempts to model the experimental data in such systems and in our laboratories utilized soot formation models from well established combustion mechanisms. We quickly realized that there are no mechanisms in the literature that serve to model the soot formation experiment data at the lower temperature conditions. Kinetic and sensitivity analysis on the mechanisms shows that the first step - that to break the first carbon - hydrogen or carbon - carbon bond is the limiting in these literature mechanisms.

We have, therefore started a search for alternative ways to generate / initiate radicals to improve the mechanisms. In this symposium we present two new initiation mechanisms and this paper focuses on one of these reactions - that of methyl radical addition to \( \pi \) bonds and substitution in SP \(^3\) Bonds of carbon to form C2 adducts which further initiate the chain and undergo further reaction to molecular weight growth.

Methyl radical, CH\(_3\), is an active species that is well known in combustion research. New results show that it can also play a role in CVD and CVI processes. We have investigated literature and performed computational chemistry calculations on addition and substitution reactions of methyl radical. Two substitution reactions are evaluated: one on aromatic and one on aliphatic systems. One reaction, addition to a \( \pi \) bond of an aromatic or olefin system, occurs via a relatively low energy barrier of only 15 kcal/mole. The second reaction, substitution in an aliphatic at a moderate energy barrier of only 50 kcal/mole, compared to bond cleavage reactions that require energies of about 100 kcal/mole. While both of these reactions are well known in gas phase kinetics, it is not clear that they have been implemented in mechanisms for evaluation of their effects. Soot formation in pyrolysis and combustion conditions occurs at sufficiently high temperatures that the substitution reaction could play a role.

Calculation Methods

Thermodynamic Properties. Geometry optimizations and frequency calculations for reactants, intermediates, and transition states from vinylidene insertion reactions are performed using several Density Functional (DFT) Methods (B3LYP/6-31G(d,p), B3LYP/6-311G(d,p), B3LYP/6-311++G(3df,2p), B3LYP/SVP and B3LYP/TZV) levels of theory in the Gaussian 98 program suite. The ab initio calculations, MP2/6-31G(d,p), MP2/full-6-311G(d,p) and G3MP2, are also used to improve our calculation level and validate the DFT results. The optimized geometry parameters with B3LYP/6-31G(d,p) level are used to obtain total electronic energies in B3LYP/6-31G(d,p), CBS-B3LYP/6-31G(d,p) single point calculations and the CBSQ/B3LYP/6-31G(d,p) composite method.

Potential Barriers for intramolecular rotation about the carbon-carbon bonds in unsaturated and polycyclic aromatic hydrocarbons are analyzed versus torsional angle using B3LYP/6-31G(d,p). Total energies are corrected by ZPVE, which are scaled by the recommended values by Scott et al.\(^1\) Thermal correction is taken into account using structures and vibrations determined at several of the calculation levels. Transition state geometries are identified by the existence of only one imaginary frequency in the normal mode coordinate analysis, evaluation of the TS geometry, the reaction coordinate vibrational motion and an intrinsic reaction coordinate analyses.

Enthalpies of formation (\( \Delta H^o_{298} \)) are estimated using total energies and calculated \( \Delta H^o_{298} \) with several isodesmic, or group balance working reactions on each species. The calculated \( \Delta H^o_{298} \) and known \( \Delta H^o_{298} \) of reference species are utilized to estimate \( \Delta H^o_{298} \) for the reference species comes from literature thermodynamic properties.

Contributions of vibration, translation, and external rotation to entropies and heat capacities are calculated by statistical mechanics based on the scaled vibrational frequencies and moments of inertia from the DFT optimized structures.

The torsion frequencies are omitted in calculation of \( S^o_{298} \) and \( Cp(T) \)'s, and their contributions are replaced with values from analysis of the internal rotations. Contributions from hindered rotors to \( S^o_{298} \) and \( Cp(T) \)'s are determined by solving the Schrödinger equation with free rotor wave functions and direct integration over energy levels of the intramolecular rotation potential curves which are represented by a truncated Fourier series expansion. The contributions from optical isomers and spin degeneracy of unpaired electrons are incorporated in S values.

Results - Thermochemical Data. The (\( \Delta H^o_{298} \)) for reactants, intermediate and products are calculated using total energies and isodesmic reactions with group balance if possible. The \( \Delta H^o_{298} \) values for transition states are calculated from the \( \Delta H^o_{298} \) values of reactants plus reaction enthalpy. Thermodynamic parameters (\( \Delta H^o_{298} \), \( S^o_{298} \) and \( Cp(300) \) to \( Cp (1500) \) for species in the reaction schemes are listed.

Kinetic Properties. Unimolecular dissociation and isomerization reactions of the chemically activated and stabilized adducts resulting from addition or combination reactions are analyzed by first constructing potential energy diagrams for the reaction system. DFT and ab initio calculations are used to calculate transition state structures and energy for isomerization, beta scission, and dissociation reactions. The enthalpies and entropies are used with conventional transition state theory to obtain high pressure limit rate constants (\( k_a \)) as a function of temperature. Nonlinear Arrhenius effects resulting from changes in the thermochemical properties of the respective transition state relative to adduct with temperature are incorporated using a two parameter Arrhenius preexponential factor (\( A, n \)) in \( A e^{nE/kT} \). Branching ratios of the energized adduct to stabilization or various product channels are then calculated using multifrequency QRRK analysis for \( k(E) \) with the steady-state assumption on the energized adduct(s). The QRRK calculation are used to evaluate energy dependent rate constants, \( k(E) \), of the energized adduct to the various channels for biomolecular chemical activation reaction systems; they include equilibrium in isomerization reactions. The QRRK / Master equation analysis described by Gilbert\(^2\), Chang et al.\(^3\) and Sheng et al.\(^4\) is shown to yield reasonable results and provides a framework by which the effects of temperature.
Results and Discussion - Reaction Paths, Barriers

One of our objectives is to show a direct reaction path that leads from methyl radicals, CH₃, over aliphatic hydrocarbons to aromatic systems. Therefore we observe some partly well known reactions and there transition states to build up a reaction path for the molecular weight growth.

Incipient with a substitution reaction of methyl radical with methane ethane and hydrogen will be formed. This transition state has a barrier of 51.24 kcal/mol and is lower than the bond dissociation in methane with 104 kcal/mol. In the next step CH₃ interacts with ethane to abstract a hydrogen and C₃H₃ and CH₄ is build over an activation barrier of ca. 14 kcal/mol.

The ethyl radical now can lose second hydrogen and our first unsaturated species is form. This takes 37.77 kcal/mol.

An additional methyl radicals react now with ethylene and produce n-propyl radical which directly can loose a hydrogen atom and forms propene. The barrier for these are 9.6 kcal/mol and 35.57 kcal/mol respectively. C₅H₅ and forms propene. The barrier of these are 9.8 kcal/mol and 35.57 kcal/mol respectively. C₅H₅ can interact with methyl in two different possibilities. One is to generate 1-butene over a H-atom substitution with a barrier of 52.24 kcal/mol. A second route leads over a quite low transition state with 1.59 kcal/mol to the allyl radical while CH₃ is produced.

1-butene can follow these recur process and the production of but-3-en-1-yl radical is conceivable. The necessary activation energy will be 15.14 kcal/mol. The abstraction of a hydrogen atom from C₅H₄ takes us to next higher homolog unsaturated hydrocarbon, 1,3-Butadiene.

Just as in the previous TST we found a 31.14 kcal/mol barrier. The following transition state shows the internal substitution of a hydrogen in z.z-2,4-Hexadien-1-yl. The barrier is with 78.19 kcal/mol lower than the methane bond energy with 104 kcal/mol.

After the formation of this cyclical hydrocarbon it is an easy exercise to make use of the introduced reaction pattern. 1,3-Cyclohexadiene will be attacked by CH₃ and loose one H atom (8.56 kcal/mol barrier).

The activation energy to loose the second hydrogen and generate the first aromatic ring is 26.56 kcal/mol. Additional CH₃ form with benzene 2-Methyl-1,4-cyclohexadienyl a subsequently toluene (12.4/43.47 kcal/mol).

The next methyl radicals can react in the following with the aliphatic or the aromatic part of toluene, which leads to a molecular weight growth on an aliphatic chain or a multi substitution of the ring.

In our study of CH₃ reactions we also analysis shift reactions to explain the formation of big graphite layers and the selective growth on the edge. In a similar pattern we start to look for 1,2-CH₃-shift reactions on small molecules till we end up with a shift reaction on top of an unsaturated ring system.

The transition states of this position change are as well investigated as the previous addition of methyl on the surface.

Conclusions

Thermodynamic properties of addition, elimination, substitution and shift reactions in the methyl system were determined by ab initio and density functional calculations. Entropies (S°) and heat capacities (Cp(T)) are also determined, with inclusion of internal rotor contributions. Reaction paths and kinetics are analyzed on methyl reaction system using QRRK for k(E) and master equation for falloff.

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References

1 Scott, A. P.; Radom, L. J. Phys. Chem. 1996, 100, 16502