Ab Initio Group Contribution Method for Activation Energies for Radical Additions

Mark Saeys, Marie-Françoise Reyniers, and Guy B. Marin
Laboratorium voor Petrochemische Techniek, Ghent University, Krijgslaan 281 S5, B-9000 Gent, Belgium

Veronique Van Speybroeck and Michel Waroquier
Laboratory of Theoretical Physics, Ghent University, B-9000 Gent, Belgium

Accurate activation energies for 67 hydrocarbon radical addition and β-scission reactions are calculated with the CBS-QB3 ab initio *method. An extension of Benson's group additivity method to activation energies is introduced. The underlying hypotheses, that is, the group concept and the additivity approximation, are validated with* ab initio *data. Standard activation group additivity values are obtained from the* ab initio *calculations for reactions involving primary, secondary, tertiary alkylic, allylic, benzylic, and vinylic radicals. The proposed group contribution method yields accurate activation energies for radical addition and for β-scission reactions. The effect of substituents on the carbon atoms of the reactive center on the activation energy can be as large as 95 kJ/mol for the adding radical, and 187 kJ/mol for the product radical of the β-scission. Non-nearest-neighbor effects such as gauche and* cis *interactions have an influence of less than 3 kJ/mol per interaction on the activation energies. However, for hydrocarbons that are heavily branched near the reactive center, these interactions can become important.*
 AIChE J, 50: 426–444, 2004
Keywords: steam cracking, ab initio calculations, CBS-QB3 method, activation energies, Benson, group additivity method

Introduction

In a continued search for higher performance, increased selectivity and faster development of new processes, the chemical industry requires accurate models with a wide range of applicability. The simulation of large-scale industrial processes is based on mathematical models that account for the chemical reactions and the physical transport phenomena that occur on the industrial scale. For an accurate description of chemical kinetics, applicable over a wide range of process conditions and for a wide range of feedstocks, a kinetic model based on elementary reactions is required.

Industrially important reactions such as partial oxidation, combustion, and the steam cracking of hydrocarbons proceed via complex radical chemistry involving hundreds of kinetically significant reaction intermediates. Building a kinetic model based on elementary reactions for such processes is a computationally challenging task. Several groups have worked on algorithms for the automated generation of complex reaction networks (Hillewaert et al., 1988; Susnow et al., 1997; De Witt et al., 2000; Wauters and Marin, 2001; Green et al., 2001; Matheu et al., 2001). Besides the demanding task to generate such networks, these kinetic models require the input of a large amount of generally unknown fundamental kinetic and thermodynamic parameters. Estimation of these parameters through the regression of experimental data puts severe limitations on the number of kinetic parameters that can be included in the kinetic model. An alternative approach to obtain quantitative values for the kinetic parameters is therefore desirable.

Correspondence concerning this article should be addressed to G. B. Marin at guy.marin@ugent.be.
Current address of M. Saeys: Dept. of Chemical and Biomolecular Engineering, National University of Singapore, 4 Engineering Drive 4, Singapore 117576.

In this work, we examine the applicability of *ab initio* quantum chemical calculations to obtain quantitative kinetic and thermodynamic data for hydrocarbon radical reactions (Heuts et al., 1996; Xiao et al., 1997; Mayer et al., 1998; Marsi et al., 2000; Sumathi et al., 2001a,b, 2002). We focus on reactions that occur during the steam cracking of hydrocarbons, though hydrocarbon radical reactions play an important role in many other chemical processes as well, ranging from atmospheric reactions to industrial processes such as combustion, polymerization, and polymer degradation. Because of the fundamental nature of the presented kinetic and thermodynamic parameters, they can be used in kinetic models for these processes as well.

The steam cracking of oil fractions is the dominant industrial source of light olefins. Steam cracking is a large-scale petrochemical process that produces up to 800,000 ton ethene and 400,000 ton propene per unit per year. Feedstocks ranging from light alkanes such as ethane and propane up to complex mixtures such as naphtha and heavy gas oil are converted at temperatures ranging from 900 K to 1200 K in tubular reactors, which are suspended in a gas-fired furnace.

The steam cracking of hydrocarbons is known to proceed through a free-radical mechanism (Rice and Herzfeld, 1934; Benson, 1960). The three main reaction families are:

(1) Carbon–carbon and carbon–hydrogen bond scissions and the reverse radical–radical recombinations

$$R_1\text{—}R_2 \rightleftharpoons R_1^{\cdot} + R_2^{\cdot}$$

(2) Hydrogen abstraction reactions, both intra- and intermolecular

$$R_1\text{—}H + R_2^{\cdot} \rightleftharpoons R_1^{\cdot} + R_2\text{—}H$$

(3) Radical additions to olefins and the reverse β-scissions of radicals, both intra- and intermolecular

$$R_1^{\cdot} + R_2{=}R_3 \rightleftharpoons R_1\text{—}R_2\text{—}R_3^{\cdot}$$

In this article we focus on the reactions in the third family, the intermolecular radical addition/β-scission reactions. During steam cracking, the monomolecular β-scission reactions determine the decomposition of the large hydrocarbons. In combination with radical addition reactions to smaller olefins, the relative rates in this family of reactions play a major role in the selectivity toward light olefins, the most important products of steam cracking.

The ever-increasing computational power and the development of better algorithms bring the accurate calculation of kinetic and thermodynamic parameters for industrially relevant gas-phase reactions from first principles within reach. Hydrocarbon free-radical reactivity and thermochemistry have been studied with a variety of computational methods, ranging from semiempirical to density functional theory (DFT) and post-Hartree-Fock methods (Wong et al., 1994; Barone and Orlandini, 1995; Heuts et al., 1996; Xiao et al., 1997; Wong and Radom, 1998; Blowers and Masel, 2000; Chuang et al., 2000; Stahl et al., 2001; Sumathi et al., 2001a,b, 2002). It is found that in order to obtain results with so-called chemical accuracy for standard enthalpies of formation, that is, better than 4 kJ/mol, calculations on radical species and on radical reactions require large basis set post-Hartree-Fock methods (Mayer et al., 1998; Chuang et al., 2000; Saeys et al., 2003).

Yet, despite the increasing computational power, it is neither possible nor desirable to calculate *ab initio* all kinetic and thermodynamic parameters that are required to model the steam cracking of hydrocarbons from first principles. First, this would require the calculation of too many kinetic parameters, even for a simple feedstock. A detailed, but far from complete reaction network for the steam cracking of C_4^- alkanes already contains about 1000 elementary reactions, and to model the cracking of naphtha and heavier feedstock, many more reactions need to be included. Second, for larger molecules accurate *ab initio* calculations become extremely demanding and the deviations with experimental reference data tend to increase with the size of the molecule. The third reason is that new time-consuming *ab initio* calculations would be required each time the reaction network is modified or enhanced to include new feedstock molecules. Clearly, an alternative method is required that can yield accurate kinetic and thermodynamic data for every possible reaction.

A variety of such methods have been put forward to obtain *thermodynamic* data. One of the most popular methods to obtain thermodynamic data is Benson's group additivity method (Benson, 1976; Cohen and Benson, 1992; 1993), in which the standard enthalpy of formation of a molecule is written as a sum of contributions for the constituting groups. The method has been successful in predicting the standard enthalpy of formation ($\Delta_f H^0$ (298 K)), the standard entropy (S^0 (298 K)), and the heat capacity ($c_p(T)$) of molecules (Cohen and Benson, 1993). As an alternative, Lay et al. (1995) have introduced hydrogen atom bond increments (HBI) for accurately estimating $\Delta_f H^0$, S^0, and $c_p(T)$ for classes of hydrocarbon radical species. The HBI technique is based on thermodynamic properties of the parent molecule, either an alkane or an alkene, and parameters for the changes in $\Delta_f H^0$, S^0, and $c_p(T)$ that occur upon formation of a radical via loss of a H atom. A third scheme was introduced by Smith (1996a,b). In his approach, the standard enthalpies of formation of alkanes and alkyl radicals are obtained from an additive bond-energy scheme, which includes additional contributions for interactions between neighboring hydrogen atoms.

Two categories of methods have also been proposed to obtain *kinetic* data. The first relates activation energies or rate coefficients to properties of the reactants and products that are accurately known experimentally or can be easily obtained. The most popular of these correlations are Evans-Polanyi relations (Evans and Polanyi, 1936; Polanyi, 1972), that is, a linear relation between the activation energy and the standard reaction enthalpy is proposed

$$E_a = E_a^0 + \gamma_p \Delta_r H^0 \tag{1}$$

Other and more accurate relations have been proposed based on Bond Order and on Valence Bond theory (Donahue et al., 1998; Zavitsas, 1998; Clarke et al., 2000; Blowers and Masel, 2000; Fischer and Radom, 2001; Shaik et al., 2001).

The second category is related to Benson's group additivity method for thermodynamic data. A first member of this cate-

gory is the structural contribution method (Willems and Froment, 1988a,b). In this method, the activation energy of a reaction is related to the activation energy of a reference reaction via contributions for the structural differences between the reactants and products of the studied reaction and the reference reaction. Estimates for these contributions were obtained by regression of experimental activation energies. The basic principles of the structural contribution method were first discussed by Kossiakoff and Rice (1943) in their seminal article on the steam cracking of hydrocarbons. An alternative approach is followed by Sumathi et al. (2001a,b, 2002). In their work, the transition state is the central concept of the method, and group additivity values (GAVs) were introduced for transition-state-specific moieties, so-called supergroups. Properties of the transition state, such as $\Delta_f H^0$, S^0, and $c_p(T)$, were calculated with accurate *ab initio* methods. Indeed, no experimental data for transition states can be obtained directly. This approach was followed for hydrogen abstraction reactions involving hydrocarbons, alcohols, aldehydes, and acids.

In this article, a method belonging to the second category will be developed. The focus will be on the activation energy, that is, the difference between the standard enthalpy of formation of the transition state and the standard enthalpy of formation of the reactants. As in the method by Sumathi et al. (2001a,b, 2002), the transition state is a central concept of the method, but the results will be cast in a format similar to the structural contribution method of Willems and Froment (1988a,b). The contributions to the activation energies will be obtained from accurate *ab initio* calculations on a large set of radical addition and β-scission reactions. First, the computational methods are discussed and the group contribution method for activation energies is derived. A database of *ab initio* activation energies is constructed and the parameters required in the group contribution method are derived. The accuracy of the new method is assessed in the sixth section. In the final part, the conclusions of this work are summarized.

Computational Methods

Ab initio molecular orbital and DFT calculations were performed with the Gaussian98 computational package (Frisch et al., 1998). Activation energies were computed with the complete basis set CBS-QB3 method (Ochterski et al., 1996; Montgomery et al., 1999, 2000). The complete basis set family of methods employs the asymptotic convergence of natural pair orbital expansions to extrapolate to the second-order Møller-Plesset (MP2) limit. Higher-order contributions are then evaluated with smaller basis sets. The most recent version of the CBS-QB3 method was used in this study (Montgomery et al., 2000). In this method B3LYP/6-311G(d,p) calculations are performed for geometry optimization and frequency calculation, and MP4(SDQ)/6-31+G(d,p) and CCSD(T)/6-31+G(d') computations to obtain the higher-order contributions to the correlation energy.

Rate coefficients can be obtained with the microscopic expression (for example, Atkins and de Paula, 2002)

$$k(T) = \kappa(T)\,\frac{k_B T V_m^0}{h}\,\frac{Q_{TS}(T)}{Q_{\text{react}}(T)}\exp\left(\frac{-\Delta E^{\neq}(0\text{ K})}{RT}\right) \qquad (2)$$

in which $\kappa(T)$ is the tunneling correction; k_B the Boltzmann constant; h the Planck constant; V_m^0 the standard molar volume; $Q_x(T)$ stands for the partition function evaluated at temperature T; and $\Delta E^{\neq}$ (0 K) is the energy difference between the reactants and the transition state, including the zero-point energy difference. Tunneling will be neglected in this work, that is, $\kappa(T) = 1$, since steam cracking occurs at a high temperature, where tunneling is less important. For the computation of accurate partition functions particular attention to internal rotations is required (Heuts et al., 1996; Irikura, 1998; Van Speybroeck et al., 2000; Sumathi et al., 2001a; Van Speybroeck et al., 2002). In this work we will, however, focus on activation energies and reaction enthalpies and we will use the rigid rotor/harmonic oscillator approximation for the partition functions.

In kinetic models for industrial reactions, Arrhenius rate coefficients, $A\exp(-E_a/RT)$, are mostly used. The Arrhenius activation energies can be obtained from the formal definition

$$E_a = RT^2\,\frac{\partial \ln k}{\partial T} \qquad (3)$$

The macroscopic formulation of the rate coefficient (e.g., Atkins and de Paula, 2002)

$$k(T) = \kappa(T)\,\frac{k_B T V_m^0}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(\frac{-\Delta H^{\neq}}{RT}\right) \qquad (4)$$

allows us to relate the Arrhenius activation energies, E_a, to the enthalpy of activation, $\Delta H^{\neq}(T)$. This results in the following expression for an ideal gas (for example, Atkins and de Paula, 2002)

$$E_a(T) = \Delta H^{\neq}(T) + (1 - \Delta n^{\neq})RT \qquad (5)$$

where $\Delta n^{\neq}$ is the change in the number of molecules in going from the reactant to the transition state, that is, $\Delta n^{\neq} = 0$ for unimolecular reactions (such as β-scission) and $\Delta n^{\neq} = -1$ for bimolecular reactions (such as radical addition). $\Delta H^{\neq}(T)$ is obtained from the CBS-QB3 calculations. In a separate study (Van Speybroeck et al., 2000, 2002) it was found that activation energies are not very sensitive to the accurate treatment of internal rotations, in contrast with preexponential factors. From Eq. 5 it follows that E_a is temperature dependent. Because of this, activation energies at 298 K and 1000 K are presented.

Recently, the modified Arrhenius rate expression, $A\,T^n\exp(-E_a/RT)$, is increasingly used by kineticists, since it more closely matches the microscopic rate expression, Eq. 2. From comparing the modified Arrhenius expression with Eq. 2, it follows that the modified Arrhenius activation energy corresponds to $\Delta E^{\neq}$ (0 K). In this article, activation energies at 0 K are reported as well to allow the activation energy of the modified Arrhenius rate expression to be determined.

In a previous article, the performance of the CBS-QB3 method for the computation of hydrocarbon thermochemistry and of kinetic parameters for different families of radical reactions was discussed (Saeys et al., 2003). It was found that after an atom additivity correction of -1.29 kJ/mol per carbon atom and -0.28 kJ/mol per hydrogen atom, CBS-QB3 yields

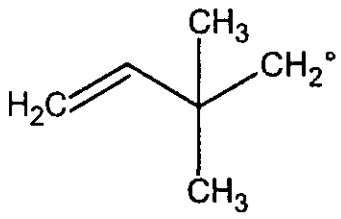


Figure 1. Benson's group additivity method: 3-dimethyl-4-but-1-enyl radical.

accurate standard enthalpies of formation with a mean absolute deviation (MAD) of 2.5 kJ/mol over a test set of 58 hydrocarbon molecules ranging from C_1 to C_{10} and consisting of alkanes, alkenes, alkynes, cycloalkanes, cycloalkenes, aromatics, and radical species. The atom additivity correction could in part be related to core correlation effects, which are not included in the CBS-QB3 method. However, this correction does not have an influence on calculated activation energies since the number of atoms does not change in going from the reactants to the transition state.

Based on a detailed study, Mayer et al. (1998) have recommended the use of their CBS-RAD method for calculations on free-radical species. This method is nearly identical to the CBS-QB3 method, but uses the more demanding QCISD/6-31G(d) method for geometry optimization and frequency calculations. Previously, we have assessed the accuracy of the B3LYP/6-311G(d,p) method, which is used in CBS-QB3 for geometry optimization, for transition state geometries (Saeys et al., 2003). B3LYP transition-state geometries were compared with IRCMax(CBS-QB3;B3LYP/6-311G(d,p)) (Malick et al., 1998) and with QCISD/6-31G(d) results. It was found that B3LYP/6-311G(d,p) slightly, but systematically, overestimates the length of the forming C–C bond. A correlation to improve the agreement was proposed. Here, we will use this correlation, Eq. 6, to improve the location of the B3LYP/6-311G(d,p) transition state.

$$\text{C–C}_{\text{IRCMax}} = 0.7381\text{C–C}_{\text{B3LYP}} + 58.03\text{pm} \quad \text{if C–C}_{\text{B3LYP}} > 225\text{pm}$$

$$\text{C–C}_{\text{IRCMax}} = \text{C—C}_{\text{B3LYP}} - 0.957\text{pm} \quad \text{if } C\text{—}C_{B3LYP} < 225\text{pm} \quad (6)$$

For larger forming C–C bond lengths, the correction becomes important, but for smaller bond lengths, the agreement between B3LYP and high-level IRCMax values is satisfactory and only a small correction is proposed. The transition state optimization is thus performed in two steps. First the transition state is fully optimized at the B3LYP/6-311G(d,p) level to determine the length of the forming C–C bond ($\text{C–C}_{\text{B3LYP}}$ in Eq. 6). Next, the transition state is reoptimized at the B3LYP/6-311G(d,p) level, this time constraining the forming the C–C bond at the improved $\text{C–C}_{\text{IRCMax}}$ length (Eq. 6). The latter geometry is used in the CBS-QB3 calculation.

Group Contribution Method for Activation Energies

Group additivity method for molecules

The standard enthalpy of formation of hydrocarbons can be determined accurately with Benson's group additivity method (Benson, 1976; Cohen and Benson, 1992, 1993). In this method a group is defined as "a polyvalent atom (ligancy ≥ 2) in a molecule together with all its ligands." A group is characterized as $X-(A)_i(B)_j(C)_k(D)_l$, where X is the polyvalent central atom, attached to i A atoms, j B atoms, and so forth. For hydrocarbons the central atom X is a carbon atom. Different types of carbon atoms are distinguished: C stands for a single-C_d for a double-, and C_t for a triple-bound carbon atom; C^* stands for a radical carbon atom and C_B for a carbon atom in a benzene ring. For example, 3-dimethyl-4-but-1-enyl (Figure 1) consists of one C_d–$(H)_2$, one C_d–(C)(H), one C–$(C^*)(C)_2(C_d)$, two C–$(C)(H)_3$, and one C^*–$(C)(H)_2$ group. For every group, a contribution to the standard enthalpy of formation of the molecule is defined. The standard enthalpy of formation of a molecule is then written as a sum of contributions for the different groups. For simplicity, contributions for non-nearest-neighbor interactions such as *gauche*, *cis*, or 1,5 interactions, which are also included in Benson's method, were neglected in our example. In Benson's group additivity method, all of the above contributions are called group additivity values (GAVs).

Group contribution method for activation energies

The standard enthalpy of formation of a transition state can be written in a completely analogous way. This requires the introduction of a number of new groups and new types of carbon atoms, next to C, C^*, C_d, C_t, and C_B. In Figure 2, the transition state of a radical addition reaction is depicted. The transition-state-specific groups are those that involve the carbon atoms C_1, C_2, or C_3. These three atoms change in carbon type during the reaction; C_1 changes from C_d to C^*, C_2 changes from C_d to C, and C_3 changes from $C^*$to C. In the transition state, these three atoms are of a carbon type that does not occur in molecules. As a result, group additivity values need to be calculated for the corresponding new groups.

These groups can be divided into three categories: (1) groups where C_1, C_2, or C_3 is the *central* atom; (2) groups where C_1,

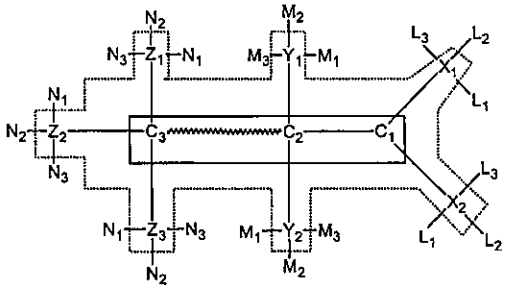


Figure 2. The transition state for a β-scission and a radical addition reaction.

The central atoms of the primary groups are enclosed by the full line. The delimitation of the reactive moiety depends on the degree to which neighbors are taken into account. The dotted line corresponds to the reactive moiety if next-nearest neighbor effects can be neglected.

Table 1. Influence of the Central Atom on the Group Additivity Values of Primary Groups in Molecules (kJ/mol)

Central Atom U:	C	$C^\bullet$	C_d
Number of Ligands n:	4	3	2
Primary group			
$U-(H)_n$	−74.9	146.6	26.2
$U-(C)(H)_{n-1}$	−41.8	160.7	35.8
$U-(C)_2(H)_{n-2}$	−20.9	171.5	42.6
$U-(C)_3(H)_{n-3}$	−10.0	171.5	n.a.
$U-(C)_4(H)_{n-4}$	0.4	n.a.	n.a.

Source: Cohen and Benson, 1993.

C_2, or C_3 is a *ligand* atom; and (3) groups related to *gauche* and *cis* interactions around C_1, C_2, and C_3. The transition-state-specific groups constitute the reactive moiety. Formally, the standard enthalpy of formation of the transition state can be written as a sum of GAVs

$$\Delta_f H^0(\mathrm{TS}) = \sum_{i=1}^{3} \mathrm{GAV}(C_i^{TS}) + \sum_{i=1}^{2} \mathrm{GAV}(X_i^{TS}) + \sum_{i=1}^{2} \mathrm{GAV}(Y_i^{TS}) + \sum_{i=1}^{3} \mathrm{GAV}(Z_i^{TS}) + \sum_{j} \mathrm{GAV}(\mathrm{NNN}_j) + \sum \mathrm{GAV} \quad (7)$$

The three categories of transition-state-specific group additivity values can be distinguished in Eq. 7. $\mathrm{GAV}(C_i^{TS})$ corresponds to the first category, $\mathrm{GAV}(X_i^{TS})$, $\mathrm{GAV}(Y_i^{TS})$, and $\mathrm{GAV}(Z_i^{TS})$ to the second, and $\mathrm{GAV}(NNN_j)$ to the third. Finally there are the non-transition-state-specific GAVs.

The first category comprises the most important groups. They can be further divided into (Figure 2; the corresponding central atoms are enclosed by the full line):

(1) *Groups with C_1 as Central Atom.* $C_1^{TS}-(C_2^{TS})(X_1)(X_2)$, where *TS* indicates the transition-state-specific carbon atom type, and X_1 are the ligand atoms of C_1^{TS}, except C_2^{TS}. They can be either a hydrogen atom or a carbon atom (that is, H, C, C_d, C_t, or C_B).

(2) *Groups with C_2 as Central Atom.* $C_2^{TS}-(C_3^{TS})(C_1^{TS})(Y_1)(Y_2)$, where Y_i indicate the ligand atoms of C_2^{TS}, except C_1^{TS} and C_3^{TS}. They can again be either a hydrogen or a carbon atom.

(3) *Groups with C_3 as Central Atom.* $C_3^{TS}-(C_2^{TS})(Z_1)(Z_2)(Z_3)$, where Z_i indicate the ligand atoms of C_3^{TS}, except C_2^{TS}. They too can be either a hydrogen or a carbon atom.

In the following, the groups of this category will be called *primary groups.* The corresponding transition-state-specific GAVs need to be determined for all these primary groups. One could try to obtain an estimate for their values from the GAVs of the corresponding groups in the reactants and product that are connected via the transition state, provided they are not too different. The required GAVs for molecules are listed in Tables 1 and 2. They were obtained from literature data (Cohen and Benson, 1993; Marsi et al., 2000). For example, during the addition of a methyl radical to ethene yielding, a 1-propyl radical (Figure 3), the GAVs for the groups with C_3, C_2, or C_1 as central atom change from, respectively, 146.6 ($C^\bullet-(H)_3$) to −41.8 kJ/mol ($C-(C)(H)_3$); from 26.2 ($C_d-(H)_2$) to −20.6 kJ/mol ($C-(C^\bullet)(C)(H)_2$); and from 26.2 ($C_d-(H)_2$) to 160.7 kJ/mol ($C^\bullet-(C)(H)_2$). These GAVs lead to a standard reaction enthalpy of −100.7 kJ/mol, whereas the experimental value is −99.0 kJ/mol (for example, Afeefy et al., 2001). The large difference between the GAVs for corresponding groups in the reactants and in the products makes it difficult to put forward an estimate for the GAVs of the corresponding groups in the transition state.

The second category of transition-state-specific groups can also be further divided (Figure 2; the corresponding central atoms are within the dotted line):

(1) *Groups with X_i as Central Atom and C_1^{TS} as a Ligand Atom.* $X_i-(C_1^{TS})(L_1)(L_2)(L_3)$, where L_i is a ligand atom of X_i and a next-nearest neighbor atom to C_1^{TS}.

(2) *Groups with Y_i as Central Atom and C_2^{TS} as a Ligand Atom.* $Y_i-(C_2^{TS})(M_1)(M_2)(M_3)$, where M_i is a ligand atom of Y_i and a next-nearest neighbor atom to C_2^{TS}.

(3) *Groups with Z_i as Central Atom and C_3^{TS} as a Ligand Atom.* $Z_i-(C_3^{TS})(N_1)(N_2)(N_3)$, where N_i is a ligand atom of Z_i and a next-nearest neighbor atom to C_3^{TS}.

The groups of this category will be called *secondary groups.* Again, we will try to obtain an estimate of the corresponding transition-state-specific GAVs by comparing the GAVs of the corresponding groups in the reactants and the products, which are connected via the transition state. The relevant GAVs for molecules are listed in Table 2. To illustrate the relative influence of the primary and secondary groups on the standard reaction enthalpy, we look at the addition of the 2-butyl radical to iso-butene forming the 2,4-dimethyl-2-hexenyl radical (Figure 4). The addition reaction leads to the following changes related to the primary groups:

- $C_3^\bullet-(C)_2(H)$ to $C_3-(C)_3(H)$: from 171.5 kJ/mol to −10.0 kJ/mol (Table 1);
- $C_{d,2}-(H)_2$ to $C_2-(C_3)(C_1^\bullet)(H)_2$: from 26.2 kJ/mol (Table 1) to −20.6 kJ/mol (Table 2);
- $C_{d,1}-(C)_2$ to $C_1^\bullet-(C_2)(C)_2$: from 42.6 kJ/mol to 171.5 kJ/mol (Table 1);

and, related to the secondary groups:

- $C-(C_3^\bullet)(C)(H)_2$ to $C-(C_3)(C)(H)_2$: from −20.6 kJ/mol to −20.9 kJ/mol (Table 2);
- $C-(C_3^\bullet)(H)_3$ to $C-(C_3)(H)_3$: from −41.8 kJ/mol to −41.8 kJ/mol (Table 2);
- $C-(C_{d,1})(H)_3$ to $C-(C_1^\bullet)(H)_3$ (twice): from −41.8 kJ/mol to −41.8 kJ/mol (Table 2).

The primary groups contribute 99.4 kJ/mol to the exothermicity of the addition reaction, while the secondary groups contribute only 0.3 kJ/mol. In general, the secondary groups will have only a minor effect on the standard reaction enthalpy because of the small difference between the corresponding reactant and product GAVs. Hence, in the first approximation,

Table 2. Influence of the Ligand Atom on the Group Additivity Values of Secondary Groups in Molecules (kJ/mol)

Ligand Atom T:	$C^\bullet$	C_d	C
Secondary group			
$C-(T)(H)_3$	−41.8**	−41.8*	−41.8*
$C-(T)(C)(H)_2$	−20.6**	−20.1*	−20.9*
$C-(T)(C)_2(H)$	−6.5**	−7.0*	−10.0*
$C-(T)(C)_3$	3.3*	7.4*	0.4*

*Cohen and Benson, 1993.
**Marsi et al. (2000).

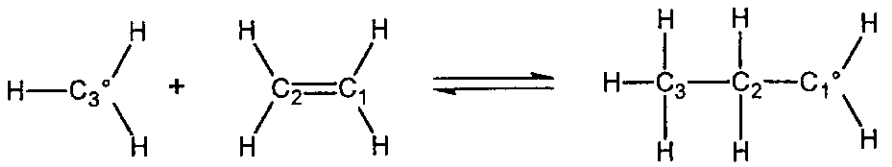


Figure 3. Methyl radical addition to ethene forming 1-propyl radical.

no distinction should be made between the reactant and product GAV of secondary groups and the corresponding transition-state-specific values.

The third category comprises GAVs for non-nearest-neighbor interactions. Also for this category, transition-state-specific GAVs are required, among others for *gauche*-like interactions between Y_i and Z_i, and between X_i and Y_i in the transition state (Figure 2). *A priori,* this category comprises a rather large number of transition-state-specific GAVs, since *gauche* and *cis* interactions can occur in various ways in the transition state. However, the corresponding GAVs for molecules are rather small (3–5 kJ/mol). Hence, the transition-state-specific GAVs can also be expected to be small and therefore differ little from the corresponding reactant and product GAV.

With the introduction of three categories of transition-state-specific groups, the standard enthalpy of formation of the transition state can be expressed (Eq. 7). The central parameters in a kinetic model are, however, the activation energies. Activation energies are obtained by taking the difference between the standard enthalpy of formation of the transition state and the standard enthalpy of formation of the reactant(s) (Eqs. 5 and 8)

$$E_a = \Delta_f H^0(TS) - \Delta_f H^0(\text{Reactants}) + (1 - \Delta n^{\neq})RT \quad (8)$$

The introduction of Eq. 7 for the standard enthalpy of formation of the transition state, as well as for the standard enthalpy of formation of the reactants into Eq. 8, leads to

$$E_a = \sum_{i=1}^{3} \Delta\text{GAV}(C_i) + \sum_{i=1}^{2} \Delta\text{GAV}(X_i) + \sum_{i=1}^{2} \Delta\text{GAV}(Y_i) + \sum_{i=1}^{3} \Delta\text{GAV}(Z_i) + \sum_{j} \Delta\text{GAV}(NNN_j) + (1 - \Delta n^{\neq})RT \quad (9)$$

where

$$\Delta\text{GAV} = \text{GAV}(TS) - \text{GAV}(\text{Reactants}) \quad (10)$$

Indeed, the non-transition-state-specific GAVs cancel out. Equation 9 defines the group contribution method. The activation energies can thus be expressed as a sum of so-called activation group additivity values, ΔGAVs. In Eq. 9, the first term corresponds to the primary contributions, the second, third, and fourth to the secondary contributions, and the fifth to the tertiary contributions.

Validity of the group contribution method for activation energies

The validity of the group-contribution method for the activation energies depends on the validity of the group additivity method for the standard enthalpy of formation of the transition state. Therefore two hypotheses must be fulfilled.

First, the validity of the *group* concept for the transition state should be assessed. This hypothesis is valid if the activation energy depends only on the structure of the reactive moiety composed of the transition-state-specific groups discussed in the previous section, that is, $C_1C_2C_3$, its neighbors, and its next-nearest neighbors (via the secondary groups). This is equivalent to neglecting non-next-nearest-neighbor effects on the activation energy, except for transition-state-specific *gauche* and *cis* interactions. If secondary and tertiary contributions to the activation energy can be neglected, the reactive moiety consists of only the primary groups and the group concept is valid. Equation 9 can be seen as a truncated series for the activation energy: the first term is the leading contribution, then follow the secondary contributions. The tertiary contributions in a way correspond to crossterms, that is, interactions between secondary groups.

Second, the *additivity* of the contributions to the activation energy should hold. This condition is more difficult to obey. In a review of radical addition reactions, Fischer and Radom (2001) have shown that there are at least two important factors that determine the activation energy of radical addition reactions. The most important is the enthalpy factor. This factor leads to a linear Evans-Polanyi-type relationship between the activation energy and the standard reaction enthalpy, Eq. 1. Since group additivity methods are found to be accurate for standard enthalpies of formation, and therefore also for stan-

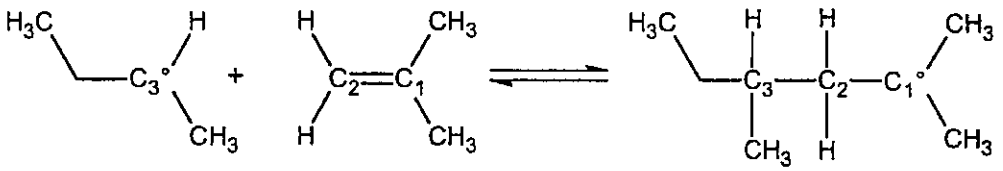


Figure 4. 2-Butyl radical addition to iso-butene forming 2,4-dimethyl, 2-hexyl radical.

dard reaction enthalpies, the applicability of the group contribution method for activation energies would be trivial if only the enthalpy factor were important. However, Fischer and Radom (2001) also stress the importance of a polar factor. Several studies on radical addition reactions have confirmed that there can be a considerable contribution from higher-lying charge-transfer states to the transition-state wave function (Donahue et al., 1998; Clarke et al., 2000; Fischer and Radom, 2001). As a result, some radicals display nucleophilic behavior and donate charge to the alkene in the transition state. Radom and Fischer (2001) propose to describe the polar effects by a multiplicative factor F_n

$$E_a = F_n \cdot (E_a^0 + \gamma_p \Delta_f H^0) \tag{11}$$

This multiplicative factor is a nonlinear s-type function determined by the difference between the ionization energy of the radical and the electron affinity of the alkene. Therefore, strong polar effects lead to an important nonlinear effect, which might invalidate the additivity of the contributions to the activation energy. Although polar effects are most important for F, Cl, CN, and O containing radicals and less important for hydrocarbon radical reactions, the tert-butyl radical is found to display nucleophilic behavior (Wong and Radom, 1994; Fischer and Radom, 2001). It has been found previously that the group additivity method for standard enthalpies of formation can fail in cases of strong, noncompensatory charge transfer from one group to its neighbors (Bader and Bayles, 2000; Sumathi et al., 2002).

Thermodynamic consistency

Thermodynamic consistency requires that the activation energy for the forward and the reverse reaction are related to the standard reaction enthalpy as in Eq. 12

$$\Delta_r H^0 = E_{a,\text{addition}} - E_{a,\beta\text{-scission}} - RT \tag{12}$$

Because of this relation only two of the three parameters can be determined independently. In this article, contributions will be determined from *ab initio* data. The computationally most efficient approach is to calculate the contributions only for the forward addition reactions (i.e., involving the smallest molecules) and obtain the contributions for the activation energies for the β-scission reactions via Eq. 12, using values for the standard reaction enthalpy. These could be calculated from tabulated, experimentally determined GAVs for the reactants and the products. This approach mixes theoretical and experimental data, and is therefore not a fully *ab initio* method anymore. Moreover, the accuracy of the kinetic data is also expected to be reduced, because (1) combining data from different sources removes the internal consistency of the data set, and (2) some of the experimental GAVs for radicals are less accurate or have not been determined. In this article, we therefore prefer to determine the contributions for the addition as well as the β-scission activation energies from *ab initio* data in order to develop a fully *ab initio* group contribution method. The reaction enthalpies obtained from the differences of the group contribution activation energies (Eq. 12) can be compared to values from Benson's group additivity method and good agreement is observed, consistent with the accurate *ab initio* standard enthalpies of formation. Of course, the presented group contribution method for addition reactions can still be combined with experimental $\Delta_r H^0$ to obtain the β-scission activation energies.

Reference reaction

The group contribution method, Eq. 9, can be made more transparent by rephrasing it. Instead of using the activation group additivity values ΔGAV directly, the activation energy can be written as the activation energy of a well-chosen reference or standard reaction plus perturbation terms that depend on the primary, secondary, and tertiary contributions,

$$E_a = E_{a,\text{Ref}} + \sum_{i=1}^{3} \Delta\text{GAV}^0(\text{C}_i) + \sum_{i=1}^{2} \Delta\text{GAV}^0(X_i) + \sum_{i=1}^{2} \Delta\text{GAV}^0(Y_i) + \sum_{i=1}^{3} \Delta\text{GAV}^0(\text{Z}_i) + \sum_{j} \Delta\text{GAV}^0(NNN_j) \tag{13}$$

The perturbation terms take into account the structural difference between the reference reaction and the studied reaction. This perturbation term is composed of standard activation group additivity values, ΔGAV^0, that is, relative to the activation energy of the reference reaction. This reformulation of the group contribution method corresponds to setting two of the primary activation group additivity values, $\Delta\text{GAV}(C_i)$, from Eq. 9, equal to zero for the reference reaction. The third one then becomes equal to the activation energy of the reference reaction. Indeed, one should realize that the three primary ΔGAVs always occur as a sum, and therefore cannot be determined independently. As an additional advantage, the leading term of the activation energy is separated from the perturbation. Since *ab initio* calculations yield more accurate relative than absolute data, the perturbation term can be expected to be even more accurate than the leading term. Moreover, most of the temperature effect on the activation energies will be taken into account through the reference activation energy, $E_{a,Ref}$. The standard activation group additivity values, ΔGAV^0, can be expected to be less temperature dependent.

Ab Initio Database of Activation Energies

In the following paragraphs, the results of *ab initio* calculations for activation energies are presented for carbon-centered radical addition reactions to alkenes and alkynes and for β-scission reactions of various radicals (Figure 5). The calculations were carried out for large sets of homologous reactions, including primary, secondary, and tertiary alkylic, allylic, benzylic, and propargylic radicals. The focus is to determine the primary standard activation group additivity values. The reactions were selected such that exactly one primary contribution can be determined from every calculated activation energy. Additional reactions were studied to estimate the importance of secondary and tertiary contributions, but a detailed treatment of these factors would require additional calculations on larger branched molecules. Although activation energies for 0, 298,

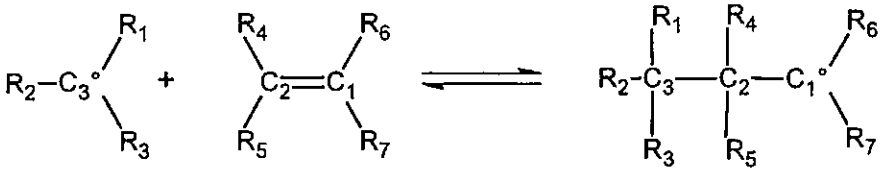


Figure 5. A radical addition and a β-scission reaction; R_i indicate alkyl substituents.

and 1,000 K are presented, the discussions will focus on the data at 1,000 K, the typical temperature during steam cracking.

Groups involving the attacking radical

In this section the influence of the structure of the attacking radical on the activation energy of the radical addition reaction is studied. For the reverse β-scission reaction, the influence of the structure of the formed radical on the activation energy is explored. To this end activation energies were calculated for a series of homologous reactions in which various types of radicals add to ethene, the major product of the steam cracking process, or in which various primary alkylic radicals undergo β-scission. Using the nomenclature of the previous section, the influence of the structure of the primary groups with carbon atom C_3 as central atom (Figures 2 and 5) on the activation energy is investigated.

To determine the primary contributions, activation energies were calculated for the addition of 19 types of radicals to ethene and for the reverse β-scission reactions (Table 3). The activation energies for the β-scission reaction of 3-phenyl-1-butyl forming ethene and a secondary benzylic radical, reaction 11 (reverse), and for the addition and β-scission involving a tertiary benzylic radical, reaction 12 (forward and reverse), were not calculated *ab initio,* since these molecules are too large for CBS-QB3 calculations. The corresponding values in Table 3 were derived in the following way. The electronic activation energies, that is, the difference in ground-state electronic energy between the transition state and the reactants, for these three reactions were obtained by adding the difference between the electronic activation energies for addition of primary allylic radicals, reaction 5, and, respectively, secondary and tertiary allylic radicals, reactions 6 and 7, to the values for the primary benzylic radical, reaction 10. This approximation is expected not to introduce much error, since these contributions are small and the allylic radicals are electronically related to the benzylic radicals. Alternatively, the contributions could be obtained from the propargylic radicals, reactions 13 to 15, but this would yield very similar results. Next, the enthalpy corrections to these electronic activation energies were obtained at the CBS-QB3 level, that is, from B3LYP/6-311G(d,p) frequency calculations.

For reaction 18, the addition of ethynyl to ethene, no transition state was found, either at the B3LYP or at the QCISD level of theory. This is consistent with the results of Stahl et al. (2001), who reported that ethynyl addition to methylacetylene is a barrierless reaction. The β-scission activation energy is given by the standard reaction enthalpy plus an RT term.

The addition activation energies vary from 0 to 95 kJ/mol, and can be divided into seven categories. The highest activation energies are found for the di-allylic radicals. The addition reaction is even endothermic for these radicals. A second group consists of the allylic radicals. A third contains the propargylic and the benzylic radicals, which display very similar reactivity. The vinylic radicals form the fourth group. Then follows the phenyl radical. The most reactive radical is the ethynyl radical. For all groups the addition of a tertiary radical proceeds with a lower barrier than the addition of a secondary, which in turn is faster than the addition of a primary radical.

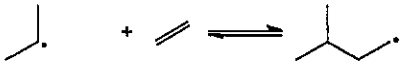
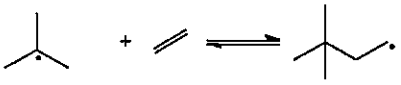
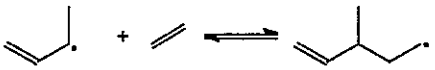
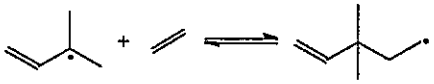
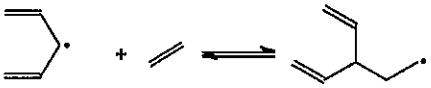
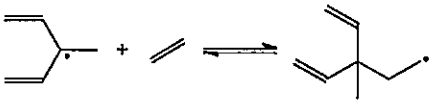
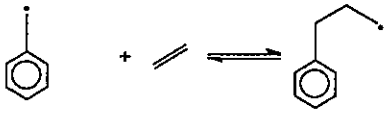
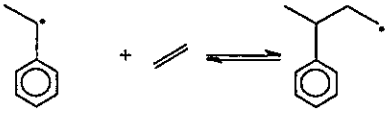
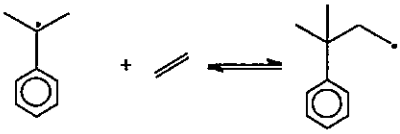
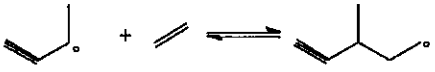
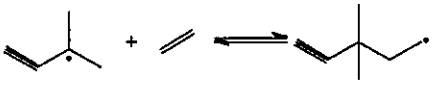
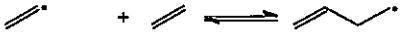
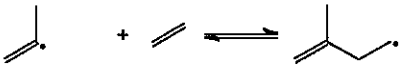
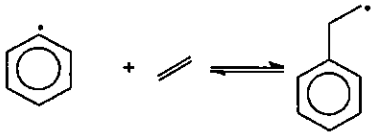
In Figure 6 the addition activation energies at 1,000 K are plotted vs. the corresponding standard reaction enthalpy. The main trend follows an Evans-Polanyi relation, Eq. 1; that is, the activation energy is lower for more exothermic reactions. However, the relative activation energies for addition of primary, secondary, and tertiary radicals do not follow this trend, namely, reactions 1 to 4; 5 to 7; 10 to 12 in Table 3 and Figure 6. In these sets of reactions, the activation energies are higher for the more exothermic reactions. The low activation energy for the addition of the *tert*-butyl radical has been reported before, based on high-level *ab initio* calculations (Wong et al., 1994; Fischer and Radom, 2001). It is believed to be caused by polar effects, which lead to a relatively strong nucleophilic character of the *tert*-butyl radical. This effect stabilizes the transition state (for example, Wong et al., 1994).

Groups involving the attacked carbon atom

In this section, activation energies are calculated for a series of β-scission reactions forming a methyl radical and an α-alkene. The reactant radical is always a primary radical and the alkyl substituents on carbon atom C_2 (Figures 2 and 5) are varied. During the β-scission the C_2–C_3 is broken and the hybridization of carbon atom C_2 changes from sp_3 to sp_2. In the reverse addition reactions, a methyl radical attacks the most alkyl substituted carbon atom of an α-alkene. The methyl radical preferentially attacks the least alkyl substituted carbon atom, but in order to study the influence of substituents at C_2, activation energies for methyl addition to the most alkyl substituted carbon atom of α-alkenes were computed here. In this way the desired standard activation group-additivity values can be retrieved from calculations on smaller molecules. As will be shown further, the results from this section can be used to obtain activation energies for reactions in which both C_1 and C_2 have alkyl substituents.

Effects of alkyl substituents at the attacked carbon atom are often explained via changes in the preexponential factors. We find that the addition activation energies vary also to a large extent, that is, by 14 kJ/mol. A similar variation is observed for the β-scission activation energies. *Ab initio* activation energies for a series of homologous reactions are listed in Table 4. Because of the early character of the addition transition state, the addition activation energy is mainly determined by steric effects of the alkyl substituents at C_2, that is, by the reorganization around C_2 from sp_2 to sp_3, and much less by the

Table 3. *Ab Initio* Activation Energies (kJ/mol) of Radical Addition and β-Scission Reactions: Influence of the Structure of the Attacking Radical

	Reaction	Radical Addition			β-Scission		
		0 K	298 K	1000 K	0 K	298 K	1000 K
1.		31.1	31.1	46.5	122.7	125.8	131.5
2.		27.3	27.9	43.7	116.3	119.0	123.4
3.		21.6	22.5	38.9	107.3	110.3	113.7
4.		14.7	15.9	33.1	96.7	100.0	102.6
5.		52.5	54.6	70.8	82.3	84.0	87.5
6.		51.0	52.7	69.1	75.9	77.7	80.3
7.		47.0	48.1	64.9	66.5	68.8	71.0
8.		75.6	78.1	94.8	55.7	60.1	57.5
9.		72.4	74.0	91.1	49.2	51.3	53.3
10.		42.2	44.9	61.2	89.2	90.9	94.5
11.		38.8	40.8	57.3	83.5*	85.0*	87.7*
12.		43.0*	41.9*	57.0*	74.3*	77.0*	79.1*
13.		43.1	44.2	60.0	87.3	89.5	93.4
14.		40.2	41.5	57.7	79.8	82.2	85.1
15.		37.2	38.0	54.8	72.2	74.8	76.9
16.		13.7	16.3	33.3	149.4	153.3	157.6
17.		10.3	13.0	30.4	138.5	142.3	145.7
18.		0.0	0.0	0.0	233.5	240.1	240.4
19.		2.5	6.4	24.2	159.4	162.2	164.8

*Estimated (see text).

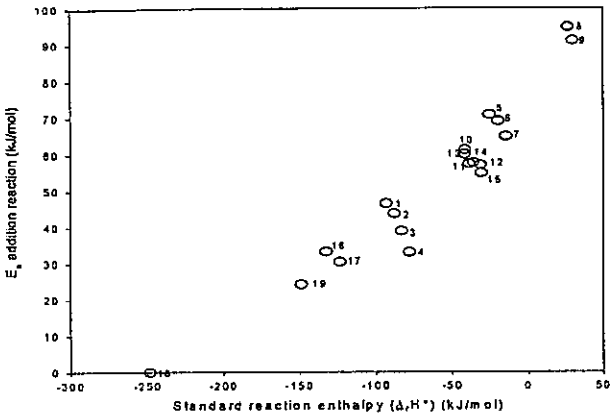


Figure 6. Evans-Polanyi plot for the addition of different radicals to ethene.

The numbers correspond to the activation energies and standard reaction enthalpies at 1000 K (Table 3).

stabilization gained by the strength of the C_3–C_2 bond. From reactions 1, 2, and 3 it follows that one methyl substituent increases the activation energy by approximately 5 kJ/mol. A vinyl substituent (reaction 4) has a slightly larger effect, but an additional methyl substituent (reaction 5) again increases the addition activation energy by 4–5 kJ/mol. A phenyl substituent (reaction 6) causes more hindering and increases the barrier by 9 kJ/mol. The activation energies for reaction 7 were estimated, since the molecule is too large for a CBS-QB3 calculation. The procedure discussed previously was used. A ethynyl substituent (reaction 8) has a slightly lower hindering effect (+3.3 kJ/mol).

The activation energy for methyl radical addition to ethyne (reaction 10) is also reported in Table 4. The barrier is slightly higher than the barrier for ethene (+3.5 kJ/mol), in agreement with data reported by Barone and Orlandini (1995). An additional methyl substituent increases the barrier by 10 kJ/mol, a vinyl substituent is again slightly less hindering (+9 kJ/mol), and an ethynyl substituent is also less hindering.

A comparison of the activation energies for the β-scission reactions indicates that they are mostly determined by the type of the carbon atom C_2 (alkyl, propargyl, allyl, or benzyl). The influence of the primary, secondary, or tertiary nature of C_2 is much smaller. The activation energy is thus dominated by the strength of the breaking C_2–C_3 bond, which is determined by the nature of the two carbon atoms. The lowest barriers are found for allylic, then propargylic, benzylic and alkylic type of C_2 atoms. This sequence parallels the C_2–C_3 bond dissociation energies.

β-Scission reactions forming an alkyne such as reactions 10 to 13 have a high barrier, consistent with the strong C–C_d bond. The rather high values for reactions 12 and 13 are probably related to the high strength of the conjugated double bond in the reactant radical.

The discussion in this section suggests that the activation energy for radical addition reactions is dominated by steric effects. These steric effects are not caused by *gauche* interactions, but by the reorganization of the substituents around the attacked carbon C_2 due to its change in hybridization from sp_2 to sp_3. Since the effect is only observed for the addition, it can be expected that the electronic reorganization is nearly complete at the transition state. Then it has the same magnitude in the reactant and in the transition state of the β-scission reaction and the effect cancels for the β-scission activation energy.

Groups involving the formed radical

In this section, the effect of the stability of the product radical on the barrier of an addition reaction is investigated. Activation energies for the addition of a methyl radical to the least alkyl substituted carbon atom of an α-alkene or -alkyne are calculated. This is the preferred addition pathway. Methyl radicals are the dominant hydrocarbon radicals and α-alkenes are the dominant alkenes in steam cracking. For β-scission reactions, the effect of the type of reactant radical on the activation energy was studied. Therefore activation energies have been calculated for a series of β-scission reactions of different types of reactant radicals forming a methyl radical and an α-alkene or -alkyne. Using the nomenclature introduced earlier, the influence of substituents at carbon atom C_1 (Figure 2 and 5) on the activation energy is investigated. The results are presented in Table 5.

The reactant radical nature (alkyl, allyl, propargyl, benzyl, or vinyl) has a large effect on activation energy for the β-scission: E_a varies from 129 kJ/mol to 201 kJ/mol. The activation energy for the methyl radical addition reaction also shows an important variation in terms of the product radical structure: from 26 kJ/mol to 52 kJ/mol.

In general, the more stable the product radical, the lower the addition barrier. A second important role is played by the stability of the reactant alkene. The high stability of butadiene causes the activation barriers for reactions 4 and 5, forming an allylic radical, to be as high as the barrier for reactions 9 and 10, forming a less stable propargylic radical. A secondary allylic radical is 15–20 kJ/mol more stable than a secondary propargylic radical. The addition activation energies at 1,000 K are plotted against the corresponding standard reaction enthalpy in Figure 7. Consistent with the arguments given here, the activation energy decreases for more exothermic reactions, but the trend is not very clear, since both the stability of the product radical and that of the reactant alkene influence the barrier and the standard reaction enthalpy.

The barriers for the reverse β-scission reactions are largely determined by the reactant radical stability. Here also a second influence can be detected that is responsible for the fine structure in the activation energies, that is, the difference between the β-scission of a secondary and of a tertiary radical, for example, reactions 2 and 3, 4 and 5, 7 and 8. Although a tertiary radical is more stable than a secondary, its β-scission activation energy is lower. This is probably caused by a *gauche* interaction that is present in all tertiary radicals and destabilizes the reactant radicals. Upon β-scission this interaction disappears, thereby lowering the activation energy. This effect also occurs for reactions 12 and 13, the β-scission of allylic radicals. The addition barriers for these two reactions follow the radical stability trend, but the β-scission barriers follow an opposite trend, caused by the *gauche* interactions present in the reactant radical. The propargylic radicals form an exception. A possible explanation is that the tertiary propargylic radical is significantly more stable than the secondary propargylic radical

Table 4. *Ab Initio* Activation Energies (kJ/mol) of Radical Addition and β-Scission Reactions: Influence of the Structure of the Attacked Carbon Atom

Reaction	Radical Addition			β-Scission		
	0 K	298 K	1,000 K	0 K	298 K	1,000 K
1. $CH_3^{\bullet}$ + 	31.1	31.1	46.5	122.7	125.8	131.5
2. $CH_3^{\bullet}$ + 	35.2	35.8	51.3	122.9	126.3	131.3
3. $CH_3^{\bullet}$ + 	40.0	40.5	56.1	122.8	126.0	130.2
4. $CH_3^{\bullet}$ + 	35.9	36.5	52.1	109.3	112.0	116.9
5. $CH_3^{\bullet}$ + 	39.9	40.6	56.4	108.9	112.0	116.9
6. $CH_3^{\bullet}$ + 	39.6	40.1	55.7	120.2	123.3	128.4
7. $CH_3^{\bullet}$ + 	43.8*	44.3*	60.0*	120.2*	123.1*	127.4*
8. $CH_3^{\bullet}$ + 	33.5	34.1	49.8	112.3	115.0	119.9
9. $CH_3^{\bullet}$ + 	39.0	39.7	55.4	113.4	116.5	121.0
10. $CH_3^{\bullet}$ + 	36.9	37.6	50.0	139.9	145.1	154.0
11. $CH_3^{\bullet}$ + 	43.8	44.9	60.1	135.8	141.1	148.7
12. $CH_3^{\bullet}$ + 	42.3	43.7	59.0	145.4	151.1	158.9
13. $CH_3^{\bullet}$ + 	42.8	43.6	56.2	136.5	141.4	149.1
14. $CH_3^{\bullet}$ + 	38.9	40.1	55.7	232.8	238.0	245.0

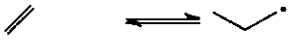
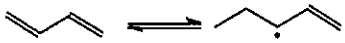
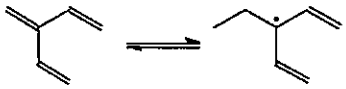
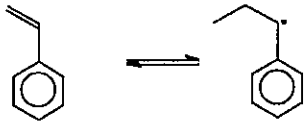
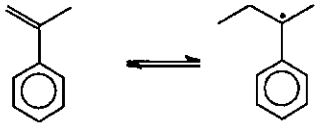
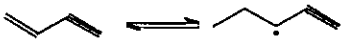
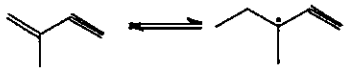
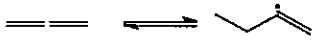
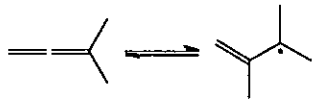
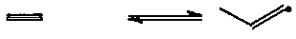
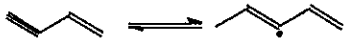
*Estimated (see text).

(by 10 kJ/mol). This difference is larger than for the allylic (7 kJ/mol) and alkylic (8 kJ/mol) radicals and seems to compensate for the *gauche* effect.

Secondary and tertiary contributions

Additional sets of reactions were studied to understand the importance of secondary contributions, that is, next-nearest-neighbor effects, and tertiary contributions, that is, *gauche* interactions. Five sets of reactions were studied: two sets to test the secondary and tertiary contributions for the attacking radical (C_3); two sets for the attacked carbon atom (C_2); and one set for the formed radical (C_1). In the discussion, we will again focus on the activation energies at 1,000 K, the typical temperature for steam cracking. The results are presented in Table 6.

Table 5. *Ab Initio* Activation Energies (kJ/mol) of Radical Addition and β-Scission Reactions: Influence of the Structure of the Formed Radical

Reaction	Radical Addition			β-Scission		
	0 K	298 K	1,000 K	0 K	298 K	1,000 K
1. $CH_3^{\bullet}$ + 	31.1	31.1	46.5	122.7	125.8	131.5
2. $CH_3^{\bullet}$ + 	29.0	30.1	45.4	122.6	125.7	132.0
3. $CH_3^{\bullet}$ + 	27.1	28.4	43.4	119.1	122.2	129.1
4. $CH_3^{\bullet}$ + 	17.1	18.3	34.0	156.9	161.4	168.6
5. $CH_3^{\bullet}$ + 	14.6	16.4	32.1	154.8	158.9	166.3
6. $CH_3^{\bullet}$ + 	7.6	9.6	25.7	187.0	192.5	200.6
7. $CH_3^{\bullet}$ + 	24.0	25.0	40.7	153.4	157.6	164.9
8. $CH_3^{\bullet}$ + 	23.1**	24.7**	40.2**	151.5**	155.7**	163.4**
9. $CH_3^{\bullet}$ + 	16.2	17.4	33.2	150.2	154.2	161.4
10. $CH_3^{\bullet}$ + 	15.3	17.1	32.7	152.6	156.2	163.5
11. $CH_3^{\bullet}$ + 	33.1	33.7	48.5	130.8	135.1	143.2
12. $CH_3^{\bullet}$ + 	34.3	36.0	51.6	231.5	236.9	243.7
13. $CH_3^{\bullet}$ + 	30.1	32.2	47.7	225.1	230.6	237.5
14. $CH_3^{\bullet}$ + 	36.9	37.6	50.0	136.9	145.1	154.0
15. $CH_3^{\bullet}$ + 	36.5	38.5	53.7	137.0	142.6	151.1
16. $CH_3^{\bullet}$ + 	22.8	24.7	40.4	169.7	174.8	182.4
17. $CH_3^{\bullet}$ + 	21.9	23.4	36.2	163.3*	167.1*	174.7*

*CBS-RAD(QCISD,B3LYP) (Mayer et al., 1998).
**Estimated (see text).

Two series of reactions were studied for the attacking radical (C_3): the addition of primary radicals (reactions 1–5), and the addition of tertiary radicals (reactions 6–8). In the latter case, the effect of secondary groups can be expected to be maximal. Five secondary groups occur in the reaction set: C–(C_3^{TS})$(H)_3$ (reaction 1), C–(C_3^{TS})(C)$(H)_2$ (reaction 2), C–(C_3^{TS})$(C)_2$(H) (reaction 3), C–(C_3^{TS})$(C)_3$ (reaction 4), and C–(C_3^{TS})$(C_B)(H)_2$ (reaction 5). Within this set, the addition and the β-scission activation energies vary by less than 4 kJ/mol. The slightly higher value for the addition activation energies for reaction 4 has a steric origin. In the transition state the *gauche* conformation is normally preferred by approximately 2 kJ/mol. This is the case for the transition states of reaction 1, 2, 3, and 5. In reaction 4, the methyl substituents destabilize this *gauche* conformation and make the *trans* conformation more preferred. This effect results in a slightly higher activation energy. For reaction 5 only the activation energy corresponding to the symmetric *trans* transition state was calculated at the CBS-QB3 level, though for this reaction the *gauche* transition state is slightly preferred at the B3LYP level. The calculation for the

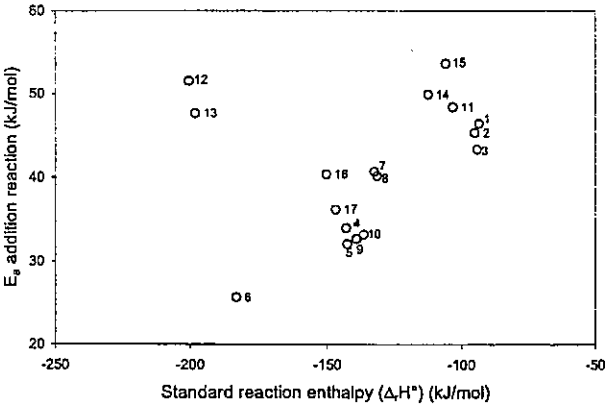


Figure 7. Evans-Polanyi plot for methyl radical addition to α-alkenes and α-alkynes.

Numbers correspond to activation energies and standard reaction enthalpies at 1000 K (Table 5).

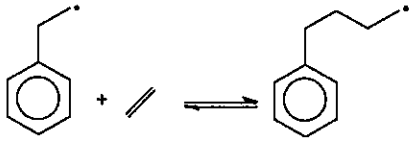
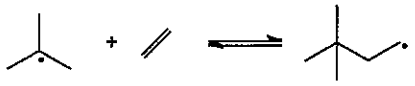
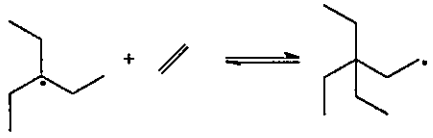
latter transition state geometry is, however, computationally too demanding at the CBS-QB3 level. The CBS-QB3 activation energies for the *gauche* transition state are therefore estimated to be approximately 2 kJ/mol lower than the reported values. The difference between the first and the fifth addition activation energy then becomes 4 kJ/mol. Considering the phenyl group is strongly electron withdrawing and the methyl group is electron donating, the difference of 4 kJ/mol is probably an upper estimate for a secondary contribution of a group with C_3 as a ligand. Note also that the standard reaction enthalpies vary by less than 5 kJ/mol, which is consistent with the data in Table 2.

For the addition of tertiary radicals (reactions 6–8) the variations are larger, since three secondary groups are involved. Three types of secondary groups are included: $C–(C_3^{TS})(H)_3$ (reaction 5), $C–(C_3^{TS})(C)(H)_2$ (reaction 6), and $C–(C_3^{TS})(C)_3$ (reaction 7). The computational demands for such calculations are very large, and reactions 7 and 8 are the largest systems that currently can be studied at the CBS-QB3 level. A second issue is that *gauche*-like interactions become important, in particular for the product of reaction 7 and the reactant, product, and transition state of reaction 8. For reaction 7, the β-scission activation energy is 6 kJ/mol higher than for reaction 6. From the difference between the activation energies for reactions 1 and 2, the secondary contribution $C–(C_3^{TS})(C)(H)_2$ can be estimated at +1.5 kJ/mol. This contribution occurs three times in reaction 7, yielding an estimated contribution of +4.5 kJ/mol. This value is in line with the *ab initio* difference of +5.9 kJ/mol between reactions 6 and 7. The addition activation energy of reaction 7 is little affected. The activation energies for reaction 8 are typical for the presence of *gauche* interactions. In the reactant there are four *gauche*-like interactions, and in the product there are six *gauche* interactions. Note that the interactions in the reactant are not genuine *gauche*-butane interactions, but so-called radical gauche interactions, that is, with a radical center at one of the middle carbon atoms (Marsi et al., 2000). According to a detailed study of Marsi et al. (2000), radical *gauche* interactions *stabilize* the radical by 0.8 kJ/mol per interaction (at 298 K). Genuine *gauche* interactions as appearing in the product *destabilize* the product by 3.0 kJ/mol per interaction (at 298 K) (Benson and Cohen, 1993). The difference in the standard reaction enthalpy for reactions 6 and 8 is 19.1 kJ/mol at 298 K. This compares well with the value obtained from the GAVs for the *gauche* interactions in the product and the reactant, that is, 6×3.0 kJ/mol $- 4 \times (-0.8$ kJ/mol$) = 21.2$ kJ/mol. According to Marsi et al. (2000), the value of 3.0 kJ/mol is probably slightly high, which would bring the estimated values even closer to the *ab initio* value. In the transition state, an intermediate GAV might be expected for the *gauche*-like interactions, say +0.8 kJ/mol at 298 K. Then the addition activation energy for reaction 8 becomes (at 298 K): 15.9 kJ/mol $- 4 \times (-0.8$ kJ/mol$) + 6 \times 0.8$ kJ/mol $= 23.9$ kJ/mol, as compared with 23.2 kJ/mol. The β-scission activation energy of reaction 8 becomes 100.0 kJ/mol $- 6 \times 3.0$ kJ/mol $+ 6 \times 0.8$ kJ/mol $= 86.8$ kJ/mol, as compared with 88.2 kJ/mol. Note that secondary contributions were neglected in this discussion.

To obtain an estimate for the secondary and tertiary contributions related to the attacked carbon atom (C_2), again two series of additional reactions were studied: addition to a secondary carbon atom (reactions 9–11) and addition to a tertiary carbon atom (reactions 12 and 13). The secondary groups change from $C–(C_{2,d})(M_1)(M_2)(M_3)$ in the reactant alkene to $C–(C_2)(M_1)(M_2)(M_3)$ in the product. From Table 2, it follows that this increases the exothermicity of the addition reaction by up to 7.0 kJ/mol, and these secondary contributions are thus expected to decrease the addition barrier and increase the β-scission barrier. Second, for larger substituents, the addition of the methyl group to C_2 increases the number of *gauche* interactions, thereby increasing the addition barrier and decreasing the β-scission barrier. Notice that the *gauche* interactions in this paragraph (such as in reactions 10, 11, and 13) are of a different type than those encountered in reaction 8 of the previous paragraph.

In going from reaction 9 to reaction 10, the addition activation energy increases by 4.1 kJ/mol, but the β-scission barrier is nearly unaffected. For reaction 10, two *gauche* interactions occur in the product and destabilize it, while the secondary contributions stabilize the product by 3.0 kJ/mol (value from Table 2). Assume that in the transition state, the double bond is still almost intact, consistent with the early transition state of the addition reaction. As a consequence, the transition state is not yet stabilized by the secondary group effect. The two *gauche* interactions between the attacking methyl radical and the two methyl groups of the reactant (3-methyl,1-butene) are, however, already partially present in the transition state and push the addition activation energy up by 4.1 kJ/mol. In proceeding from the transition state to the product, the two *gauche* interactions further increase (from +4.1 to $2 \times +3.0 = +6.0$ kJ/mol), but the secondary effects stabilize the product (−3.0 kJ/mol). The β-scission barrier is therefore little affected: the *gauche* contributions, which lower the activation energy (−1.9 kJ/mol), are approximately compensated by the loss of stabilization due to secondary groups (+3.0 kJ/mol). For reaction 11, a similar reasoning can be followed. In this case, four *gauche* interactions develop during the radical addition reaction, pushing the addition activation energy up even higher (+4.9 kJ/mol). The stabilization effect is also larger for this reaction (−7.0 kJ/mol from Table 2). The β-scission barrier for this reaction is slightly lowered, probably due to the high number of *gauche* interactions, which have a larger influence

Table 6. *Ab Initio* Activation Energies (kJ/mol) for Radical Addition and β-Scission Reactions: Influence of Secondary and Tertiary Contributions

	Reaction	Radical Addition			β-Scission		
		0 K	298 K	1,000 K	0 K	298 K	1,000 K
1.		27.3	27.9	43.7	116.3	119.0	123.4
2.		26.4	27.8	43.7	117.8	120.5	124.9
3.		24.5	26.1	42.1	115.5	118.1	122.5
4.		27.5	29.1	45.0	117.6	120.0	124.5
5.		24.5*	26.1*	42.0*	119.4*	121.9*	126.4*
6.		14.7	15.9	33.1	96.7	100.0	102.6
7.		14.0	14.8	31.8	103.6	106.2	108.5
8.		22.6	23.2	40.5	88.8	88.2	94.5
9.	$CH_3^{\bullet}$ + 	35.2	35.8	51.3	122.9	126.3	131.3
10.	$CH_3^{\bullet}$ + 	39.3	39.8	55.4	123.3	126.4	131.4
11.	$CH_3^{\bullet}$ + 	40.0	40.6	56.2	122.9	125.8	130.7
12.	$CH_3^{\bullet}$ + 	40.0	40.5	56.1	122.8	126.0	130.2
13.	$CH_3^{\bullet}$ + 	45.1	45.4	61.3	121.0	123.4	127.3
14.	$CH_3^{\bullet}$ + 	29.0	30.1	45.4	122.6	125.7	132.0
15.	$CH_3^{\bullet}$ + 	28.4	29.6	44.9	120.7	129.0	130.4

*Symmetric *trans* transition state.

than the loss of the secondary stabilization. The barriers for reactions 12 and 13 again illustrate this.

Finally, the importance of secondary contributions related to the formed radical (C_1) was tested briefly (reactions 14 and 15). Only a small effect is expected, since the differences between the GAVs for C–($C_{3,d}$)(N_1)(N_2)(N_3) and C–(C_3^*)(N_1)(N_2)(N_3) are 0.0, −0.5, +0.5, and −4.1 kJ/mol (Table 2). The addition barrier decreases slightly, and the β-scission barrier is lowered slightly more. The latter might be partially caused by a *gauche* interaction in the reactant radical.

To summarize: secondary contributions related to C_3 are typically smaller than 5 kJ/mol, secondary contributions related to C_2 are typically smaller than 3 kJ/mol, and secondary contributions related to C_1 are even smaller. Tertiary contributions of the types discussed in this section—some additional types will be encountered later—lower the β-scission activation energy by 2–3 kJ/mol per interaction and increase the addition activation energy by less than 1–2 kJ/mol per interaction. Therefore, secondary and tertiary contributions to the activation energy can often be neglected to a first approximation. They can, however, become important for reactions involving heavily branched molecules.

Standard Activation Group Additivity Values

In the previous section, a database of *ab initio* activation energies was constructed. In this section, the standard activation group additivity values, $\Delta GAV^0(C_i)$, for the group contribution method, Eq. 13, will be derived from this database. As was shown, secondary and tertiary contributions can to a first approximation be neglected in the group contribution method. Equation 13 can therefore be simplified, retaining only the three primary contributions

$$E_a = E_{a,Ref} + \Delta GAV^0(C_1) + \Delta GAV^0(C_2) + \Delta GAV^0(C_3) \quad (14)$$

This formulation resembles that of Willems and Froment (1988a,b), and situates the latter within the framework of Benson's group additivity method. The main difference is that the method of Willems and Froment only emphasises the structure of the reactant and product radical, that is, C_1 and C_3, to determine the activation energy.

The decomposition of 1-propyl is taken as the reference reaction for the β-scission reactions, and the methyl addition to ethene, the reverse reaction, is taken as the reference reaction for the radical addition reactions (Figure 3). These are the smallest molecules in the homologous sets, and it would be possible to do highly accurate quantum chemical calculations for these reactions or to use accurate experimental data. The standard activation group additivity values, $\Delta GAV^0(C_i)$, are obtained from Tables 3, 4, and 5, by taking the difference between the activation energy for the reaction in which the particular $\Delta GAV^0(C_i)$ occurs and the activation energy of the reference reaction.

To illustrate the procedure, an example will be given for each of the three types of primary standard activation group additivity values. The standard activation group additivity value at 1,000 K for C_3–(C_d)($C)_2$, that is, for an attacking radical carbon atom with two alkylic and one vinylic carbon atom as ligands, is obtained from the difference between the activation energy for reaction 7 from Table 3 and the activation energy for the reference reaction, reaction 1. For the addition reaction, this yields 64.9 − 46.5 = +18.4 kJ/mol; for the β-scission reaction, it yields 71.0 − 131.5 = −60.5 kJ/mol. The standard activation group additivity value for C_2–(C_t)(H), that is, for an attacked carbon atom with a ethynylic carbon atom and a hydrogen atom as ligands, is found from reaction 8, Table 4. For the addition reaction, a $\Delta GAV^0(C_2)$ of 49.8 − 46.5 = +3.3 kJ/mol is obtained. For the β-scission reaction, 119.9 − 131.5 = −11.6 kJ/mol is calculated. The standard activation group additivity value for C_1–(C_d)$_2$, that is, for a formed carbon atom with two vinylic carbon atom as ligands, is found from reaction 6, Table 5. For the addition reaction $\Delta GAV^0(C_1)$ = 25.7 − 46.5 = −20.8 kJ/mol, and for the β-scission reaction $\Delta GAV^0(C_1)$ = 200.6 − 131.5 kJ/mol = +69.1 kJ/mol.

All the standard activation group additivity values for activation energies at 1000 K are reported in Table 7. Standard activation group additivity values for activation energies at 0 K and at 298 K can be obtained analogously from Tables 3, 4, and 5.

Validation and Application of the Group Contribution Method

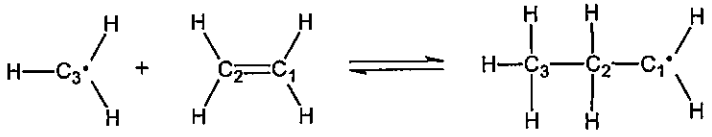
The standard activation group additivity values derived in the previous section can be used in the group contribution method to calculate activation energies for reactions that were not included in the *ab initio* database. To test the validity of the method, group contribution activation energies are compared with CBS-QB3 *ab initio* values in Table 8. Because of the limited size of the molecules that can be calculated with CBS-QB3, only systems involving two contributions in Eq. 14 are tested. Moreover, if three contributions are involved, *gauche* and/or *cis* interactions could become more important. Such reactions are therefore not good test reactions, since this type of interaction is not yet included in the present method.

The first activation energy in Table 8 is calculated using two contributions from Table 7: C_2–(C_d)(H) and C_1–(C)(H). The agreement with the CBS-QB3 values is very good. The activation energy for reaction 3 is obtained by combining the reference activation energy with contributions for C_3–(C)$(H)_2$, $C_{2,t}$–(H), and $C_{1,t}$–(C). The agreement is also fairly good for this reaction. Reaction 4 is chosen as a test case where polar effects are important: the *tert*-butyl radical displays nucleophilic behavior and butenyne can be considered electrophilic. Yet, the group contribution activation energies are in agreement with the *ab initio* values. The *ab initio* values are slightly lower, which might be attributed to additional polar stabilization of the transition state.

Some cases where the group contribution method does not yield accurate activation energies can also be found in Table 8: for reaction 6, the *ab initio* addition activation energy is substantially lower than the group contribution value. This is caused by two *cis* interactions that destabilize the reactant alkene and lower the activation barrier. Also the high value for the β-scission barrier seems to be caused by two partial *cis* interactions in the transition state. Normally, a lower *ab initio* barrier is expected due to *gauche* interactions in the reactant. However, in the transition state the *gauche* interactions change

Table 7. Standard Activation Group Additivity Values (kJ/mol) for the Group Contribution Method for Carbon-Centered Radical Addition and β-Scission Activation Energies at 1,000 K

Reference reaction:



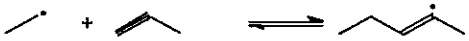
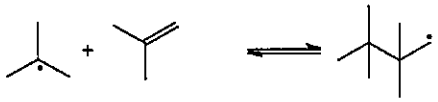
Reference Reaction Activation Energy	Addition Reaction 46.5 ΔGAV^0	β-Scission Reaction 131.5 ΔGAV^0
Groups involving C_3		
1. C_3–(C)$(H)_2$	−2.8	−8.2
2. C_3–$(C)_2$(H)	−7.5	−17.8
3. C_3–$(C)_3$	−13.3	−29.0
4. C_3–$(C_d)(H)_2$	+24.3	−44.0
5. C_3–(C_d)(C)(H)	+22.6	−51.2
6. C_3–$(C_d)(C)_2$	+18.4	−60.5
7. C_3–$(C_d)_2$(H)	+48.3	−71.4
8. C_3–$(C_d)_2$(C)	+44.6	−78.3
9. C_3–$(C_B)(H)_2$	+14.7	−37.0
10. C_3–(C_B)(C)(H)	+10.8	−43.8*
11. C_3–$(C_B)(C)_2$	+10.5*	−52.4*
12. C_3–$(C_t)(H)_2$	+13.5	−38.1
13. C_3–(C_t)(C)(H)	+11.2	−46.4
14. C_3–$(C_t)(C)_2$	+8.1	−54.7
15. $C_{3,d}$–(H)	−13.2	+26.1
16. $C_{3,d}$–(C)	−16.0	+14.1
17. $C_{3,t}$	−46.5**	+108.5**
18. $C_{3,B}$	−22.3	+33.2
Groups involving C_2		
1. C_2–(C)(H)	+4.8	−0.2
2. C_2–$(C)_2$	+9.6	−1.3
3. C_2–(C_d)(H)	+5.7	−14.6
4. C_2–(C_d)(C)	+9.9	−15.2
5. C_2–(C_B)(H)	+9.2	−3.1
6. C_2–(C_B)(C)	+13.5*	−4.1*
7. C_2–(C_t)(H)	+3.3	−11.6
8. C_2–(C_t)(C)	+8.9	−10.5
9. $C_{2,t}$–(H)	+3.5	+22.5
10. $C_{2,t}$–(C)	+13.6	+17.2
11. $C_{2,t}$–(C_d)	+12.6	+27.4
12. $C_{2,t}$–(C_t)	+9.7	+17.6
13. $C_{2,allene}$	+9.2	+113.5
Groups involving C_1		
1. C_1–(C)(H)	−1.1	+0.5
2. C_1–$(C)_2$	−3.1	−2.4
3. C_1–(C_d)(H)	−12.4	+37.1
4. C_1–(C_d)(C)	−14.4	+34.8
5. C_1–$(C_d)_2$	−20.8	+69.1
6. C_1–(C_B)(H)	−5.8	+33.4
7. C_1–(C_B)(C)	−6.3*	+31.9*
8. C_1–(C_t)(H)	−13.3	+29.8
9. C_1–(C_t)(C)	−13.8	+32.0
10. $C_{1,allene}$–(C_d)	+2.0	+11.7
11. $C_{1,alleneII}$–(C)(H)	−4.1	−1.3
12. $C_{1,alleneII}$–$(C)_2$	−8.0	−7.5
13. $C_{1,t}$–(C)	+3.7	−2.9
14. $C_{1,t}$–(C_d)	−9.6	+28.4
15. $C_{1,t}$–(C_t)	−13.8	+20.7

*Estimated.
**No classic TST.

to *cis* interactions, which are more destabilizing. This effect increases the β-scission barrier.

Also for reaction 7, substantial differences are seen. Here, *gauche* interactions cause the increase of the addition barrier and the decrease of the β-scission barrier. Also, for reactions 4 and 5, some *gauche* interactions occur, but they have a much smaller effect, and the group contribution activation energies are in good agreement with the *ab initio* values.

Table 8. *Ab Initio* (AI) and Group Contribution (GC) Activation Energies (kJ/mol) of Radical Addition and β-Scission Reactions at 1,000 K

Reaction	Radical Addition		β-Scission	
	AI	GC	AI	GC
1. $CH_3^{\bullet}$ + 	50.1	51.1	118.1	117.4
2. 	30.3	31.3	160.0	160.4
3. 	52.8	50.9	144.5	142.9
4. 	16.1	19.9	131.2	132.3
5. 	31.8	30.1	102.7	100.1
6. $CH_3^{\bullet}$ + 	45.5	53.0	135.7	127.8
7. 	50.9	42.8	90.8	101.2

So, in the absence of non-nearest-neighbor interactions such as *cis* and *gauche* interactions, the group contribution method yields activation energies within 3 kJ/mol of the *ab initio* result, even in the presence of polar effects. However, the presence of multiple *gauche* interactions can increase the addition barrier by up to 10 kJ/mol and decrease the β-scission barrier by a similar amount. *Cis* interactions have the opposite effect: they destabilize the alkene and decrease the addition barrier, but increase the β-scission barrier.

Conclusions

Many important chemical transformations occur via complex radical reaction networks. The accurate simulation of such processes requires fundamental kinetic models, comprising a large number of elementary reactions. The fundamental nature of the elementary reactions allows calculating the required kinetic parameters from first principles. A kinetic database for the family of hydrocarbon radical addition/β-scission reactions has been constructed by applying the CBS-QB3 *ab initio* method.

An extension of Benson's group-additivity method to activation energies was developed. This new method can yield accurate activation energies for every possible reaction within the family, based on a limited number of parameters, so-called standard activation group additivity values, that can be determined from the *ab initio* kinetic database. It is thermodynamically consistent and, in principle, does not require any experimental data. However, the use of a reference reaction for each family allows the introduction of experimental information or data from computationally very demanding *ab initio* methods in a flexible way without compromising the rigor of the method. In a first approximation the required standard activation group additivity values are related to the primary groups, that is, next-nearest-neighbor effects are neglected.

The developed group contribution method allows an *ab initio* description of the complex reaction network describing the chemistry of industrial processes such as steam cracking of hydrocarbons. Indeed, it is not limited to the radical addition/β-scission reactions, but can be applied in a straightforward way to the other important steam cracking reaction families, such as carbon–carbon scissions and hydrogen abstractions.

An extension of the group contribution method to heteroatom-containing hydrocarbons, such as Cl-, F-, and O-, can be envisaged.

Acknowledgment

One of the authors (M.S.) is grateful to the Fund for Scientific Research-Flanders, Belgium (F.W.O.-Vlaanderen) for a Research Assistantship.

Notation

CBS-QB3 = complete basis set method (Montgomery et al., 2000)
CCSD(T) = coupled cluster single-and-double theory with a quasi-perturbative correction for triple contributions
c_p = heat capacity, J/mol K
DFT = density functional theory
E_a = Activation energy, J/mol
$E_{a,Ref}$ = Activation energy of the reference reaction within the group contribution method, J/mol
E_a^0 = Evans-Polanyi parameter, J/mol
$\Delta E^{\neq}(0\ K)$ = activation energy at 0 K, J/mol
GAV = Group additivity value, J/mol
$\Delta GAV(X_i)$ = activation group additivity value for a group with central atom X_i, J/mol
$\Delta GAV^0(X_i)$ = standard activation group additivity value for a group with central atom X_i, J/mol
h = Planck constant, 6.62608×10^{-34} J s
$\Delta_f H^0$ = standard enthalpy of formation, J/mol

$\Delta H^{\neq}$ = difference between the $\Delta_f H^0$ for the transition state and the $\Delta_f H^0$ for the reactant(s), J/mol
$\Delta_r H^0$ = standard reaction enthalpy, J/mol
k = reaction rate coefficient, $m^3 mol^{-1} s^{-1}$ or s^{-1}
k_B = Boltzman constant, 1.3807×10^{-23} J K^{-1}
MP2 = second order Møller-Plesset perturbation theory
MP4(SDQ) = fourth order Møller-Plesset perturbation theory without contributions from triply excited determinants
$\Delta n^{\neq}$ = change in number of molecules in going from the reactant(s) to the transition state
QCISD = quadratic configurational interaction with all single and double excited states
Q_x = partition function for X, m^{-3}
R = gas constant, 8.3145 J/mol K
S^0 = standard entropy, J/mol K
$\Delta S^{\neq}$ = activation entropy, J/mol K
T = temperature, K
TS = transition state
V_m^0 = standard molar volume, m^3/mol

Greek letters

γ_p = Evans-Polanyi factor
$\kappa(T)$ = tunneling constant

Literature Cited

Afeefy, H. Y., J. F. Liebman, and S. E. Stein, "Neutral Thermochemical Data," *NIST Chemistry WebBook,* NIST Standard Reference Database Number 69, P. J. Linstrom, and W. G. Mallard, eds., National Institute of Standards and Technology, Gaithersburg, MD, 20899, (2001). (http://webbook.nist.gov)

Atkins, P. W., and J. de Paula, *Physical Chemistry,* 7th ed., Oxford Univ. Press, Oxford (2002).

Bader, R. F. W., and D. Bayles, "Properties of Atoms in Molecules: Group Additivity," *J. Phys. Chem. A,* **104,** 5579 (2000).

Barone, V., and L. Orlandini, "Methyl Addition to Acetylene and Ethene from a Density Functional Approach," *Chem. Phys. Lett.,* **246,** 45 (1995).

Benson, S. W., *The Foundations of Chemical Kinetics,* McGraw-Hill, New York (1960).

Benson, S. W., *Thermochemical Kinetics,* 2nd ed., Wiley, New York (1976).

Blowers, P., and R. Masel, "Engineering Approximations for Activation Energies in Hydrogen Transfer Reactions," *AIChE J.,* **46,** 2041 (2000).

Chuang, Y.-Y., E. L. Coitiño, and D. G. Truhlar, "How Should We Calculate Transition State Geometries for Radical Reactions? The Effect of Spin Contamination on the Prediction of Geometries for Open-Shell Saddle Points," *J. Phys. Chem. A,* **104,** 446 (2000).

Clarke, J. S., H. A. Rypkema, J. H. Kroll, N. M. Donahue, and J. G. Anderson, "Multiple Excited States in a Two-State Crossing Model: Predicting Barrier Height Evolution for H + Alkene Addition Reactions," *J. Phys. Chem. A,* **104,** 4458 (2000).

Cohen, N., and S. W. Benson, "The Thermochemistry of Alkanes and Cycloalkanes," *The Chemistry of Alkanes and Cycloalkanes,* S. Patai, and Z. Rappoport, Eds., Wiley, New York (1992).

Cohen, N., and S. W. Benson, "Estimation of Heats of Formation of Organic Compounds by Additivity Methods," *Chem. Rev.,* **93,** 2419 (1993).

De Witt, M. J., D. J. Dooling, and L. J. Broadbelt, "Computer Generation of Reaction Mechanisms Using Quantitative Rate Information: Application to Long-Chain Hydrocarbon Pyrolysis," *Ind. Eng. Chem. Res.,* **39,** 2228 (2000).

Donahue, N. M., J. S. Clarke, and J. G. Anderson, "Predicting Radical-Molecule Barrier Heights: The Role of the Ionic Surface," *J. Phys. Chem. A,* **102,** 3923 (1998).

Evans, M. G., and M. Polanyi, "Further Considerations on the Thermodynamics of Chemical Equilibria and Reaction Rates," *Proc. Roy. Soc. A,* **154,** 133 (1936).

Fischer, H., and L. Radom, "Factors Controlling the Addition of Carbon-Centered Radicals to Alkenes—An Experimental and Theoretical Perspective," *Angew. Chem. Int. Ed.,* **40,** 1340 (2001).

Frisch, M. J., G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, *Gaussian 98* Rev. A.7, Gaussian, Inc., Pittsburgh (1998).

Green, W. H., Jr., P. I. Barton, B. Bhattacharjee, D. M. Matheu, D. A. Schwer, J. Song, R. Sumathi, H.-H. Carstensen, A. M. Dean, and J. M. Grenda, "Computer Construction of Detailed Chemical Kinetic Models for Gas-Phase Reactors," *Ind. Eng. Chem. Res.,* **40,** 5370 (2001).

Heuts, J. P. A., R. G. Gilbert, and L. Radom, "Determination of Arrhenius Parameters for Propagation in Free-Radical Polymerizations: An Assessment of ab Initio Procedures," *J. Phys. Chem.,* **100,** 18997 (1996).

Hillewaert, L. P., J. L. Dierickx, and G. F. Froment, "Computer Generation of Reaction Schemes and Rate Equations for Thermal Cracking," *AIChE J.,* **34,** 17 (1988).

Irikura, K. K., "Essential Statistical Thermodynamics," *Computational Thermochemistry: Prediction and Estimation of Molecular Thermodynamics,* ACS Symp. Ser., Vol. 677, K. K. Irikura, and D. J. Frurip, eds., American Chemical Society, Washington, DC, pp. 402–418 (1998).

Kossiakoff, A., and F. O. Rice, "Thermal Decomposition of Hydrocarbons, Resonance Stabilization and Isomerization of Free Radicals," *J. Amer. Chem. Soc.,* **65,** 590 (1943).

Lay, T. H., J. W. Bozzelli, A. M. Dean, and E. R. Ritter, "Hydrogen Atom Bond Increments for Calculation of Thermodynamic Properties of Hydrocarbon Radical Species," *J. Phys. Chem.,* **99,** 14514 (1995).

Malick, D. K., G. A. Petersson, and J. A. Montgomery, Jr., "Transition States for Chemical Reactions I. Geometry and Classical Barrier Height," *J. Chem. Phys.,* **108,** 5704 (1998).

Marsi, I., B. Viskolcz, and L. Seres, "Application of the Group Additivity Method to Alkyl Radicals: An ab Initio Study," *J. Phys. Chem. A,* **104,** 4497 (2000).

Matheu, D. M., T. A. Lada, W. H. Green, Jr., A. M. Dean, and J. M. Grenda, "Rate-Based Screening of Pressure-Dependent Reaction Networks," *Comput. Phys. Commun.,* **138,** 237 (2001).

Mayer, P. M., C. J. Parkinson, D. M. Smith, and L. Radom, "An Assessment of Theoretical Procedures for the Calculation of Reliable Free Radical Thermochemistry: A Recommended New Procedure," *J. Chem. Phys.,* **108,** 604 (1998).

Montgomery, J. A., Jr., M. J. Frisch, J. W. Ochterski, and G. A. Petersson, "A Complete Basis Set Model Chemistry. VI Use of Density Functional Geometries and Frequencies," *J. Chem. Phys.,* **110,** 2822 (1999).

Montgomery, J. A., Jr., M. J. Frisch, J. W. Ochterski, and G. A. Petersson, "A Complete Basis Set Model Chemistry. VIII. Use of the Minimum Population Localization Method," *J. Chem. Phys.,* **112,** 6532 (2000).

Ochterski, J. W., G. A. Petersson, and J. A. Montgomery, Jr., "A Complete Basis Set Model Chemistry. V. Extensions to Six or More Heavy Atoms," *J. Chem. Phys.,* **104,** 2598 (1996).

Polanyi, J. C., "Some Concepts in Reaction Dynamics," *Acc. Chem. Res.,* **5,** 161 (1972).

Rice, F. O., and K. F. Herzfeld, "Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. VI. The Mechanism of Some Chain Reactions," *J. Amer. Chem. Soc.,* **56,** 284 (1934).

Saeys, M., M.-F. Reyniers, G. B. Marin, V. Van Speybroeck, and M. Waroquier, "Ab Initio Calculations for Hydrocarbons: Enthalpy of Formation, Transition State Geometry and Activation Energy for Radical Reactions," *J. Phys. Chem. A,* **107,** 9147 (2003).

Shaik, S., W. Wu, K. Dong, L. Song, and P. C. Hiberty, "Identity Hydrogen Abstraction Reactions, $X^0 + H{-}X' \rightarrow X{-}H + X'^0$ ($X{=}X'{=}CH_3$, SiH_3, GeH_3, SnH_3, PbH_3): A Valence Bond Modeling," *J. Phys. Chem. A,* **105,** 8226 (2001).

Smith, D. W., "Adaptive Bond Energy Schemes for the Calculation of Enthalpies of Formation and Bond Dissociation Energies for Alkyl Radicals," *J. Chem. Soc., Faraday Trans.,* **92,** 4415 (1996a).

Smith, D. W., "Adaptive Bond-Energy Schemes for the Calculation of Enthalpies of Formation of Hydrocarbons Including Geminal H-H Terms," *J. Chem. Soc., Faraday Trans.,* **92,** 1141 (1996b).

Stahl, F., P. v. R. Schleyer, H. F. Bettinger, R. I. Kaiser, Y. T. Lee, and H. F. Schaefer III, "Reaction of the Ethynyl Radical, C_2H, with Methy-

lacetylene, CH_3CCH, Under Single Collision Conditions: Implications for Astrochemistry," *J. Chem. Phys.*, **114,** 3476 (2001).
Sumathi, R., H.-H. Carstensen, and W. H. Green, Jr., "Reaction Rate Predictions via Group Additivity, Part 1: H Abstraction from Alkanes by H and CH_3," *J. Phys. Chem. A,* **105,** 6910 (2001a).
Sumathi, R., H.-H. Carstensen, and W. H. Green, Jr., "Reaction Rate Predictions via Group Additivity, Part 2: H-Abstraction from Alkenes, Alkynes, Alcohols, Aldehydes, and Acids by H Atoms," *J. Phys. Chem. A,* **105,** 8969 (2001b).
Sumathi, R., H.-H. Carstensen, and W. H. Green, Jr., "Reaction Rate Predictions via Group Additivity, Part 3: Effect of Substituents with CH_2 as the Mediator," *J. Phys. Chem. A,* **106,** 5474 (2002).
Susnow, R. G., A. M. Dean, W. H. Green, Jr., P. Peczak, and L. J. Broadbelt, "Rate-Based Construction of Kinetic Models for Complex Systems," *J. Phys. Chem. A,* **101,** 3731 (1997).
Van Speybroeck, V., D. Van Neck, M. Waroquier, S. Wauters, M. Saeys, and G. B. Marin, "Ab Initio Study of Radical Addition Reactions: Addition of a Primary Ethylbenzene Radical to Ethene (I)," *J. Phys. Chem. A,* **104,** 10939 (2000).
Van Speybroeck, V., D. Van Neck, and M. Waroquier, "Ab Initio Study of Radical Reactions: Role of Coupled Internal Rotations on the Reaction Kinetics (III)," *J. Phys. Chem. A,* **106,** 8945 (2002).
Wauters, S., and G. B. Marin, "Computer Generation of a Network of Elementary Steps for Coke Formation During the Thermal Cracking of Hydrocarbons," *Chem. Eng. J.,* **82,** 267 (2001).
Willems, P. A., and G. F. Froment, "Kinetic Modelling of the Thermal Cracking of Hydrocarbons. 1. Calculation of Frequency Factors," *Ind. Eng. Chem. Res.,* **27,** 1959 (1988a).
Willems, P. A., and G. F. Froment, "Kinetic Modelling of the Thermal Cracking of Hydrocarbons. 2. Calculation of Activation Energies," *Ind. Eng. Chem. Res.,* **27,** 1966 (1988b).
Wong, M. W., A. Pross, and L. Radom, "Addition of *tert*-Butyl Radical to Substituted Alkenes: A Theoretical Study of the Reaction Mechanism," *J. Amer. Chem. Soc.,* **116,** 11938 (1994).
Wong, M. W., and L. Radom, "Radical Addition to Alkenes: Further Assessment of Theoretical Procedures," *J. Phys. Chem. A,* **102,** 2237 (1998).
Xiao, Y., J. M. Longo, G. B. Hieshima, and R. J. Hill, "Understanding the Kinetics and Mechanism of Hydrocarbon Thermal Cracking: An Ab Initio Approach," *Ind. Eng. Chem. Res.,* **36,** 4033 (1997).
Zavitsas, A. A., "Energy Barriers to Chemical Reactions. Why, How, and How Much? Non-Arrhenius Behavior in Hydrogen Abstractions by Radicals," *J. Amer. Chem. Soc.,* **120,** 6578 (1998).

Manuscript received Jan. 23, 2003, and revision received June 10, 2003.