# Factors Controlling the Addition of Tert-Butyl Radical to 1,2-disubstituted and 1,1,2-trisubstituted Alkenes

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(**Received:** 2 /4 / 2008 ---- **Accepted:** 5 / 1 / 2010)

## Abstract

Within the frame of this work the factors that determine the rate of addition of tert-butyl radical to 1,2-disubstituted and 1,1,2-trisubstituted alkenes are investigated. Some electronic properties of the two carbons involved in addition reaction were calculated using quantum-mechanical methods.These carbon are the less-substituted methylene carbon of the alkene and the carbon bearing the single electron of the tert-butyl radical. The electronic density of the highest occupied molecular orbital (HOMO) of alkene,the electronic density of the lowest unoccupied molecular orbital(LUMO) of the alkene and the total electronic density of the single occupied orbital (SOMO) of the tert-butyl radical. The rate constants of the addition reaction of tert-butyl radical with alkenes are correlated with the above mentioned physical properties of tert butyl radical and alkenes using astatistical program in order to determine the factors controlling the addition reaction.

**Keywords :** radical addition reactions,polar effects,enthalpy effects, abinitio calculations.

## Introduction

Radical addition reaction have fundamental importance in many areas of chemistry, e.g radical polymerization and organic synthesis .Afrequently raised question in the literature is what are the dominant factors influencing radical addition reactions? Experimental studies[1-2] emphasize the importance of polar effects while theoretical calculation[3-5] show anumber of instances where enthalpy effects are more important or at least as important as polar effects. Recently Random et al. Published high-level abinitio quantum chemical calculations[6-10] on radical addition reactions. They concluded that free radical is primarily governed by both polar and enthalpy effects.

In the present work ,quantum mechanical calculations have been carried out for some important electronic properties of two carbons involved in the addition reaction ,namely ,the less-substituted methylene carbon of the alkene and the carbon bearing the single electron of the tert-butyl radical . The steric energy for the transition complex is also calculated for the case where the two carbons involved in the addition reaction approach each other with adistance of 2A$^{o}$ .The electronic properties include the total electronic densities of the two carbons and the HOMO,LUMO and SOMO energy levels .The single and multiple linear regression analysis was used to establish correlation between the rate constant as dependent variable and the above mentioned physical properties as independent variables.

## Calculations

MOPAC:Was applied to obtain some physical properties of alkenes and tert – butyl radical . These properties include the electron densities of the various atoms and the energy levels of HOMO, LUMO and SOMO .These data are calculated from the most stable configuration obtained by energy minimization procedures using AM1.

MM2: The steric energy of the tert-butyl radical and the alkene was obtained using MM2 for the case transition state of the addition reaction**.**

SPSS:The statistical program was applied to establish correlation between the rate of addition of tert-butyl redical to alkenes and the physical properties of the involved alkenes and tert-butyl radical.

## Results and Discussion

Table(1) gives some relevant physical properties of some 1-2-disubstituted and 1, 1, 2-trisubstituted alkenes. These calculated physical properties: the total electron density on the less substituted methylene carbon.the HOMO energy level,the LUMO energy level on the activation energy. The compounds are arranged according to increased total electron density on the less substituted methylene carbon.

Table (2) gives the calculated relevant physical properties of the tert-butyl radical. These properties the total electron density on the carbon bearing the single electrone of the free radical and the SOMO energy level.

**Table(1): physical properties of some 1,2-disubstituted and 1,1,2-trisubsituted alkenes CHA=CXY**

| Alkene | X | Y | A | Total ED | $E_{HOMO}$ (e.v) | $E_{LUMO}$ (e.v) | EA |
|---|---|---|---|---|---|---|---|
| | H | Ph | (E) - CN | 4.0941 | -9.86084 | -0.03929 | |
| | H | $Co_2Me$ | (E)- $Co_2Me$ | 4.1096 | -11.43582 | -0.99976 | |
| | H | $Co_2Me$ | (Z)- $Co_2Me$ | 4.1109 | -11.41544 | -0.54877 | |
| | Cl | Cl | Me | 4.1415 | -9.77166 | 0.37298 | 5.1 |
| | H | Ph | (E)-Me | 4.1477 | -9.43100 | 0.50577 | |
| | Cl | Cl | Cl | 4.1530 | -9.95551 | -0.06075 | 6.6 |
| | H | Cl | (Z)- Cl | 4.1583 | -9.97279 | 0.37587 | 5.3 |
| | H | Me | (Z)- Me | 4.1676 | -9.54121 | 1.29398 | -5.3 |
| | Me | Me | Me | 4.1693 | -9.26336 | 1.22328 | 2.8 |
| | H | Ph | (E) - $Co_2Me$ | 4.1981 | -9.43687 | -0.69587 | |
| | H | Cl | (E)- Cl | 4.2180 | -10.55159 | 1.43784 | 0.6 |

**E and Z isomers**
**Total ED:Total electron density on less substituted methylene carbon.**
**$E_{HOMO}$:Energy level of HOMO.$E_{LUMO}$:Energy level of LUMO**
**EA: Activation energies**

**Table 2. Physical properties of tert-butyl radical**

| **Free Radical** | **EDR** | **E SOMO** |
|---|---|---|
| $C(CH_3)_3$ | 4.2135 | -11.96351 |

EDR: Electron density of the carbon bearing the single electron of the tert-butyl radical
E SOMO: Energy level of SOMO.

If the electronic density of the carbon bearing The single electron is higher than the electron density of all substitute carbons of the involved alkenes , the tert-butyl radical behaves as anucleophilic agent and the rate of addition increases as the electron density of less substituted carbons of alkene decreases Table (3) gives the rate constant of the addition of tert-butyl radical to alkenes[11]

**Table 3. log rate constant K($M^{-1} S^{-1}$) of the addition tert-butyl radical to alkenes**

| **Alkene (X,Y,A)** | | | **Radical** $C(CH_3)_3$ |
|---|---|---|---|
| Cl | Cl | Me | 0.005 |
| H | Ph | (E)-Me | 0.014 |
| H | Me | (Z)- Me | 0.033 |
| Cl | Cl | Cl | 0.048 |
| H | $Co_2Me$ | (Z)- $Co_2Me$ | 0.070 |
| H | Cl | (Z)-Cl | 0.085 |
| Me | Me | Me | 0.11 |
| H | $Co_2Me$ | (E)- $Co_2Me$ | 0.18 |
| H | Cl | (E)-Cl | 0.23 |
| H | Ph | (E)- $Co_2Me$ | 1.1 |
| H | Ph | (E)-CN | 2.8 |

**Table (4):steric energy ( K cal, mole) for the radical-alkene complex in the transition state**

| **Alkene (X,Y,A)** | | | **Radical** $C(CH_3)_3$ |
|---|---|---|---|
| H | Ph | (E)-CN | 18.0168 |
| H | Ph | (E)-Me | 18.8263 |
| Me | Me | Me | 25.6543 |
| H | Me | (Z)- Me | 25.8122 |
| H | Ph | (E)- $Co_2Me$ | 26.6655 |
| Cl | Cl | Me | 27.3078 |
| H | Cl | (Z)-Cl | 27.5890 |
| H | Cl | (E)-Cl | 28.4670 |
| Cl | Cl | Cl | 30.8025 |
| H | $Co_2Me$ | (E)- $Co_2Me$ | 38.8200 |
| H | $Co_2Me$ | (Z)- $Co_2Me$ | 42.9497 |

Table (4). gives the steric energies for the transition state complexes between the free radical and alkenes. It is well established that substitution of one or both methylene hydrogen atoms of a monosubstituted or 1,1- disubstituted alkene $CH_2$=CXY by other atoms or groups change the overall rate constant of aradical addition. In most cases substitution at the attacked site lowers the rate constants. This is commonly attributed to asteric substituent effect which hinders the approach of the radical and acomparison of the rate constants and the activation parameters for the addition to alkenes CHA=CXY and $CH_2$ =CXY In the chosen examples the attack at the less substituted carbon atom is always strongly preferred.

**Table 5. results of the regression analysis for the addition of tert-butyl radical to alkenes**

| Model No. | Model | a | R | $R^2$ |
|---|---|---|---|---|
| 1 | Constant<br>Activation Energy | 9.099E-02<br>-2.31E-03 | 0.127 | 0.016 |
| 2 | Constant<br>HOMO Energy Level | 1.994<br>0.156 | 0.140 | 0.020 |
| 3 | Constant<br>LUMO Energy Level | 0.492<br>-0.259 | 0.252 | 0.064 |
| 4 | Constant<br>Total Electron Density | 30.662<br>-7.283 | 0.322 | 0.104 |
| 5 | Constant<br>Steric Energy | 1.875<br>-5.13E-02 | 0.447 | 0.200 |
| 6 | Constant<br>Activation Energy<br>Total Electron Density | -13.552<br>6.168E-03<br>3.268 | 0.986 | 0.973 |
| 7 | Constant<br>Activation Energy<br>Steric Energy<br>Total Electron Density | -14.032<br>8.425 E-03<br>-7.32 E-03<br>3.431 | 0.995 | 0.990 |

a: Regression coefficient, R: correlation coefficient

Table(5) shows that the correlation of the log rate constants of the addition of tert-butyl radical with the single parameters.Total electron density, HOMO and LUMO energy level , steric and the activation energy gives correlation coefficients in the range (0.1-0.4). Total electron density and activation energy taken together give acorrelation coefficient of (0.986). The polar,steric and activation energy factors give together agood correlation coefficient of (0.995) The activation energy ,polarity, steric and the energy levels of the frontier orbitals are the important factor that control the rate of addition tert-butyl radical to alkenes.

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# العوامل المؤثرة على إضافة جذر البيوتيل الثالثي الى الالكينيات الثنائية وثلاثية التعويض

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## الملخص

تم في سياق هذا البحث دراسة العوامل المؤثرة في سرعة اضافة جذر بيوتيل ثالثي الى عدد من مشتقات الايثين ثنائية التعويض و ثلاثية التعويض لما لهذا الموضوع من اهمية في تفسير فاعلية المركبات الالكينية تجاه عمليات البلمرة المستهلة بالجذور الحرة تم حساب عدد من الصفات الالكترونية للكاربونين اللذين يشتركان في عملية اضافة الجذر الحر الى الالكين باستخدام طرق ميكانيك الكم. وكذلك تم حساب مستويات الطاقة لاوربيتالات SOMO,LUMO,HOMO واستخدمت طريقة احصائية لربط هذه الصفات الالكترونية مع ثوابت معدل السرع النسبية للاضافة وظهرت بأن عوامل الاستقطابية وطاقة التنشيط ومستوى طاقة LUMO,HOMO عوامل رئيسية في تحديد ثابت سرعة اضافة جذر بيوتيل ثالثي الى الالكينات .