THEORETICAL STUDIES ON THE RECOMBINATION REACTION OF
tert-BUTYL RADICALS

T. KÖRTVÉLYESI and L. SERES

Institute of Physical Chemistry, Attila József University,

P.O.Box 105, H–6701 Szeged, Hungary

THE SELF—COMBINATION OF THE *tert*—BUTYL RADICALS (C_{3v}) WAS STUDIED THEORETICALLY AT THE LEVEL OF SEMIEMPIRICAL QUANTUM CHEMICAL METHODS, BY MEANS OF UHF—MINDO/3 AND UHF——AM1, WITH COMPLETE GEOMETRICAL OPTIMIZATION. THE MINIMUM ENERGY REACTION PATH (MERP), AND THE STRUCTURE AND ENERGY OF THE TRANSITION STATE WERE DETERMINED. INCORRECT ACTIVATION AND BOND DISSOCIATION ENERGIES, COMPARED WITH THE EXPERIMENTAL RESULTS, WERE OBTAINED BY MEANS OF UHF APPROXIMATIONS. UHF APPROXIMATION IS NOT ACCEPTABLE TO DESCRIBE THE COMBINATION OF LARGE RADICALS WITH HIGH SYMMETRY.

Introduction

The kinetic and thermochemical characteristics of the *tert*-butyl radical have attracted much attention during the past twenty years. The structure of the radical was studied at the level of *ab initio* quantum chemical calculations by PACANSKY *et al.* [1]. A structure with C_{3v} symmetry was found to be the most stable. The IR spectrum of the radical was also consistent with C_{3v} symmetry [2]. Thus, the structure and the thermochemistry of the radical are well established [3–7].

The recombination reaction has been studied experimentally in different laboratories and the logarithm of the preexponential factor was found to be between 8.4 and 12.38 [8–11]. In the evaluation of the kinetic results in a 400 K temperature interval, McMILLEN and GOLDEN [3] concluded, that the self–combination has zero activation energy. TSANG [12] came to the same conclusion. Laser Induced Fluoro-

escence experimental results were published recently by ANASTASI and ARTHUR [13,14]. A small negative activation energy ($E_A = -0.5$ kJ mol^{-1}) was found.

The self—combination reaction of the methyl radical has been studied in detail at the *ab initio* level [15,16] and by semiempirical SCF—MO methods (UHF—MINDO/3, UHF—MNDO, MNDO—CI, UHF—AM1 and AM1/CI) (*e.g.*[17,18]). The minimum energy reaction path (MERP) calculated by means of UHF—MINDO/3 and UHF—AM1 [19, 20] has no barrier, but the bond dissociation energies (BDEs) were found to be less than the experimental ones. DANNENBERG *et al.* [18] proposed the method of MNDO including configuration interaction (CI 3x3 — open shell excited singlet) and an extended CI (9x9, 27x27, 57x57) method for the combination of radicals containing heteroatoms with lone electron—pairs to model the combination of small alkyl radicals. By the UHF approximation of MNDO and AM1 the combination reactions of large alkyl radicals has not so far been studied. It is of interest to examine whether semiempirical quantum chemical methods with UHF approximation predict acceptable results for the combination of larger radical(s) with high symmetry. The combination of *tert*—butyl radicals was studied in detail and some results are presented here.

Results and Discussion

Our UHF—MNDO and UHF—AM1 calculations on the geometry of the dissociating ethane molecule predict two independent methyl structures at a distance of circ. 230 pm on the MERP. From this distance the energy decreases by less than 0.4 kJ mol^{-1} at every 10 pm. The self—combination of the *tert*—butyl radical can be regarded as that of a substituted methyl radical. The effect of the methyl groups on the self—combination was investigated at the level of semiempirical quantum chemical methods, by means of UHF—MINDO/3 and UHF—AM1 of AMPAC [19]. The MERPs

were investigated in the reverse (bond cleavage) direction, starting from the optimal geometry of 2,2,3,3–tetramethylbutane with the symmetry of D_{3h} (see Fig.1). The calculation of the MERP in the bond forming direction was not successful because of SCF–convergency problems (at around 500 pm) and spin–separation problems (at around 300 pm).
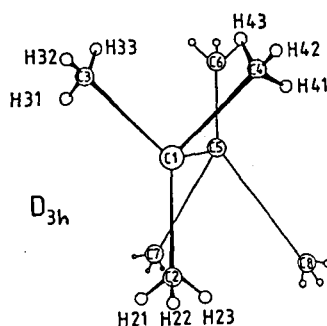

Figure 1: The structure of the reactant in the decomposition reaction of 2,2,3,3–tetramethylbutane (D_{3h})

The calculated MERPs are depicted in Figure 2. The MERP of A–TS–B was calculated by UHF–MINDO/3, and A'–TS'–B' by UHF–AM1. The geometry of the transition state (TS) was established by means of the McIVER–KOMORNICKI method [20] with the keyword of SIGMA [19].

The energies of the reactant (*tert*–butyl radical), the transition state and the product (2,2,3,3–tetramethyl–butane) calculated *via* UHF–MINDO/3 and UHF–AM1, together with the experimentally determined [21] and thermochemically calculated data [22], are included in Table I. The activation energies of the self–combination calculated by UHF–MINDO/3 and UHF–AM1 are 168.2 and 46.5 kJ mol⁻¹, respecti-
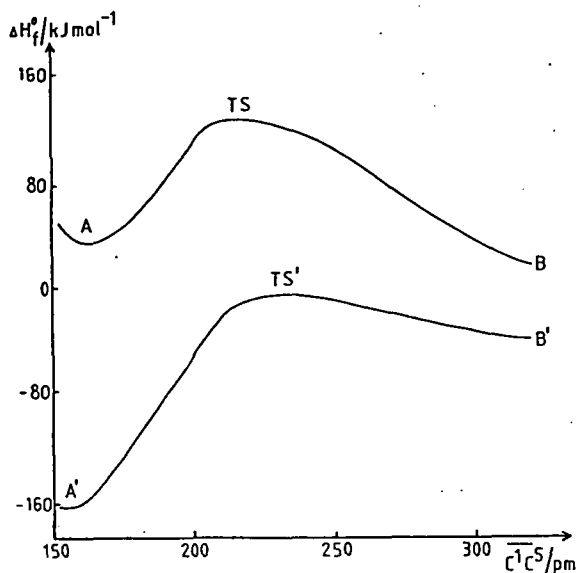
Figure 2. The MERPs of the recombination reaction of *tert*–butyl radicals.
A–TS–B was calculated by UHF–MINDO/3 and A'–TS'–B' by
UHF–AM1

vely. The former method gives an unrealistically high value which can be due to the
number of electron repulsion integrals being reduced greatly by using the core
approximation [23]. The calculated energies of the molecules containing crowded
(*tert*–butyl) groups are inadequately described by MINDO/3 calculations [23,24]. The
activation energies of the C–C bond cleavage reaction are 91.2 kJ mol^{-1} (UHF–
–MINDO/3) which is evidently an underestimation of the C–C bond strength. UHF–
–AM1 predicts BDE(*tert*–C_4H_9–*tert*–C_4H_9) = 163.9 kJ mol^{-1} which is an acceptable

result related to the experimental one (158.8 kJ mol^{-1} [21,22]).

The geometries in the TS calculated by means of UHF–MINDO/3 and UHF–AM1 are summarized in Table II. The central bond distances (C^1C^5) in the TS calculated by UHF–MINDO/3 and UHF–AM1 differ by 10.8 pm. The spin contamination in the direction of the TS is increased, the spin separation begins at circ. 200 pm. AM1/CI 3x3 (open shell excited singlet) method predicts good MERPs (BDEs and activation energies) for the combination of small and medium size alkyl and alkenyl radicals [25]. Further calculations are in progress by means of this method.

Table I

Heats of formation of the reactant (*tert*–butyl radical), the TS and the product (2,2,3,3–tetramethylbutane) calculated by UHF–MINDO/3 and UHF–AM1

Heats of formation/kJ mol^{-1}	UHF–MINDO/3	UHF–AM1	Exp.[20,21]
tert–butyl radical	−22.1	−26.7	48.6
transition state	124.0	−6.9	—
2,2,3,3–tetramethylbutane	32.8	−170.8	−61.6

Conclusion

The calculated distance between the developing radical centres in the TS is approximately of 230 pm which is close to the C–C bond distance at nearly full spin separation in the decomposition of ethane. Both the activation energy of the bond formation and breaking are much greater and less, respectively, than those of the experimental results at UHF–MINDO/3 approximation for the combination of radicals with tertiary carbon radical centre. UHF–AM1 predicts a good BDE, but an unrealistically high activation energy.

Table II

Geometry of the TS of *tert*–butyl radical recombination
(see Figure 1)

Geometry	UHF–MINDO/3	UHF–AM1
C^1C^5/pm	220.3	231.7
C^1C^2/pm	150.7	147.9
C^1C^3/pm	150.7	147.9
C^1C^4/pm	150.7	147.9
C^2H^{21}/pm	111.4	112.1
C^2H^{22}/pm	111.1	111.7
C^2H^{23}/pm	111.1	111.7
$\Theta(C^2C^1C^5)$	105.5	109.6
$\Theta(C^3C^1C^5)$	105.5	111.2
$\Theta(C^4C^1C^5)$	105.5	111.2
$\delta(C^2C^1C^5C^6)$	179.7	179.5
$\delta(C^3C^1C^5C^6)$	60.3	60.3
$\delta(C^4C^1C^5C^6)$	59.7	61.2

Acknowledgement

References

[1]   *Pacansky, J., M.Yoshimine:* J.Phys.Chem. *90*, 1980 (1986).

[2]   *Pacansky, J., J.S.Chang:* J.Chem.Phys. *74*, 5539 (1981).

[3]   *McMillen, D.F., D.M.Golden:* "Hydrocarbon Bond Dissociation Energies" in Annual Reviews of Physical Chemistry, .S.Rabinowitch, Ed.;Annual Rewiews Inc., Palo Alto, CA, p.493, 1982.

[4]   *Russell, J.J., J.A.Seetula, R.S.Timonen, D.Gutman, D.F.Nava:* J.Amer.Chem.Soc. *110*, 3084 (1988).

[5] *Tsang, W.:* In "Shock Waves in Chemistry", A.Lifshitz, Ed.;Marcel Dekker, New York, 1981, p.59.

[6] *Walker, J.A., W.Tsang:* Int.J.Chem.Kinet., *11,* 867 (1967).

[7] *Atri, G., R.R.Baldwin, G.A.Evans, R.W.Walker:* J.Chem.Soc., Faraday Trans.I. *74,* 366 (1978).

[8] *Golden, D.M., Z.B.Alfassi, P.C.Beadle:* Int.J.Chem.Kinet. *6,* 359 (1974).

[9] *Parkes, D.A., C.P.Quinn:* J.Chem.Soc., Faraday Trans. I. *72,* 1952 (1976).

[10] *Choo, K., P.C.Beadle, L.W.Piszkiewicz, D.M.Golden:* Int.J.Chem.Kinet. *8,* 45 (1976).

[11] *Kerr, J.A., S.J.Moss:* "Handbook of Bimolecular and Termolecular Gas Reactions", CRC Press, Inc. Boca Raton, Florida, 1981.

[12] *Tsang, W.:* J.Amer.Chem.Soc. *107,* 2872 (1985).

[13] *Anastasi, C., N.L.Arthur:* J.Chem.Soc. Faraday Trans. II. *83,* 277 (1987).

[14] *Arthur, N.L.:* J.Chem.Soc., Faraday Trans.II. *82,* 1057 (1986).

[15] *Carlacci, L.,C.Doubleday,Jr., T.R.Furlani, H.F.King, J.W.McIver,Jr.:* J.Amer.Chem.Soc. *109,* 5323 (1987).

[16] *Darvesh, K.V., R.J.Boyd, P.D.Pacey:* J.Phys.Chem. *93,* 4772 (1989).

[17] *Dannenberg, J.J., J.C.Rayez, M.T.Rayez−Meaume, P.Halvick:* J.Mol.Struct. *123,* 343 (1985).

[18] *Körtvélyesi, T., L. Seres:* React. Kinet. and Catal. Lett., in press.

[19] a.) Dewar Research Group, and *J.J.P.Stewart:* QCPE Bull. *6,*

24 (1986)., b.) QCPE Program 506.

[20]   *Komornicki, A., J.W.McIver:* J.Amer.Chem.Soc. *94*, 2625 (1972).

[21]   *Russell, J.J., J.A.Seetula, R.S.Timonen, D.Gutman, D.F.Nana:* J.Amer.Chem.Soc. *110*, 3084 (1988).

[22]   *Seres, L., L.Zalotai, F.Márta:* Acta Phys.et Chem. Szeged, *23*(4), 433 (1977).

[23]   *Bingham, R.C., M.J.S.Dewar, D.H.Lo:* J.Amer.Chem.Soc. *97*, 1294 (1975).

[24]   *Dewar, M.J.S., W.Thiel:* J.Amer.Chem.Soc. *99*, 4907 (1977).

[25]   *T.Körtvélyesi, L.Seres:* J.Mol.Struct. (THEOCHEM), accepted for publication.