

Addition of *tert*-Butyl Radical to Substituted Alkenes: A Theoretical Study of the Reaction Mechanism

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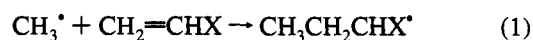
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Abstract: High-level ab initio calculations at the QCISD/6-311G** + ZPVE level have been carried out to study the addition reactions of *tert*-butyl radical to a set of substituted alkenes, CH₂=CHX (X = H, NH₂, F, Cl, CHO, and CN), and the results analyzed with the aid of the curve-crossing model. The reactivity of the *tert*-butyl radical is found to be governed by a combination of enthalpy and polar factors. The polar factor leads to *tert*-butyl radical displaying strong nucleophilic character which stabilizes the transition states by 20–25 kJ mol⁻¹ compared with those for the relatively nonpolar reactions of methyl radical. Consequently, barrier heights are significantly lower for radical addition reactions of *tert*-butyl (1.9–21.6 kJ mol⁻¹) than for methyl (24.3–39.8 kJ mol⁻¹). A transition state structure–enthalpy correlation is found for the addition reactions of *tert*-butyl radical but is shifted slightly from the correlation line previously found for the CH₃[•], CH₂OH[•], and CH₂CN[•] radicals, reflecting the increasing importance of polar contributions.

Introduction

The rate of addition of radicals to alkenes has been studied extensively and it has been postulated to be governed by a complex interplay of polar, enthalpy, and steric effects.² However, establishing the relative importance of these factors in specific cases has proven to be quite difficult.^{3,4} In recent work, we have found that a combination of high level ab initio calculations, together with a curve-crossing analysis, is effective

in assessing the relative importance of polar and enthalpy factors for reactions in the gas phase.⁵ Thus, for the addition of methyl radical to monosubstituted alkenes:



we came to the surprising conclusion that, contrary to the generally accepted viewpoint, polar interactions did not significantly affect the barrier height and the reaction was primarily governed by enthalpy effects.^{5a,b} In contrast, a corresponding study of the addition reactions of the substituted methyl radicals, CH₂OH[•] and CH₂CN[•], indicated a large polar contribution.^{5c} The CH₂OH[•] radical was found to be nucleophilic in character, while CH₂CN[•] was found to be electrophilic in character, although the reactivity of both radicals appeared to be strongly influenced by reaction enthalpy as well. Accordingly, CH₂OH[•] and CH₂CN[•] showed significantly lower barrier heights than CH₃[•] at a given reaction enthalpy due to the stabilizing influence of the charge-transfer configurations for these two radicals.^{5c}

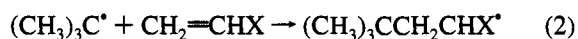
A point of further interest in these earlier studies was the observation that, while the reactions of CH₃[•] and CH₂OH[•] with CH₂=CHX led to *individual* barrier height–enthalpy correlations, the set of three radicals showed no global correlation,^{5c} a plot of barrier height against enthalpy for the radicals CH₃[•], CH₂OH[•], and CH₂CN[•] was one of total scatter. Remarkably, however, this set of three radicals did show a global transition state (TS) structure–enthalpy correlation. This intriguing result was rationalized^{5c} with the aid of the curve-crossing model.⁶

(5) (a) Wong, M. W.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1993**, *115*, 11050. (b) Wong, M. W.; Pross, A.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 415. (c) Wong, M. W.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1994**, *116*, 6284.

(6) For reviews of the curve-crossing model, see: (a) Pross, A.; Shaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363. (b) Pross, A. *Adv. Phys. Org. Chem.* **1985**, *21*, 99. (c) Shaik, S. S. *Prog. Phys. Org. Chem.* **1985**, *15*, 197. (d) Shaik, S. S. *Acta Chem. Scand.* **1990**, *44*, 205. (e) Shaik, S. S.; Schlegel, H. B.; Wolfe S. *Theoretical Aspects of Physical Organic Chemistry, The S_N2 Transition State*; Wiley: New York, 1992.

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 (2) For reviews, see: (a) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 753. (b) Tedder, J. M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 401. (c) Tedder, J. M.; Walton, J. C. *Adv. Free Radical Chem.* **1980**, *6*, 155. For a recent thorough analysis of the mechanistic aspects of radical addition reactions, see: (d) Heberger, K.; Fischer, H. *Int. J. Chem. Kinet.* **1993**, *25*, 249.
 (3) For recent experimental studies on the importance of polar effects in the addition reactions of substituted methyl radicals, see: (a) Mungler, K.; Fischer, H. *Int. J. Chem. Kinet.* **1985**, *17*, 809. (b) Beranek, I.; Fischer, H. In *Free Radicals in Synthesis and Biology*; Minisci, F., Ed.; Kluwer: Dordrecht, 1989. (c) Fischer, H. In *Free Radicals in Synthesis and Biology*; Viehe, H. G., Janousek, Z., Merenyi, R., Eds.; Reidel: Dordrecht, 1986. (d) Heberger, K.; Walbinder, M.; Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 635. (e) Fischer, H.; Paul, H. *Acc. Chem. Res.* **1987**, *20*, 200. (f) Avila, D. V.; Ingold, K. U.; Luszytyk, J.; Dolbier, W. R.; Pan, H.-Q. *J. Am. Chem. Soc.* **1993**, *115*, 1577. (g) Citterio, A.; Sebastiano, R.; Marion, A.; Santi, R. *J. Org. Chem.* **1991**, *56*, 5328. (h) Riemenschneider, K.; Bartels, H. M.; Dornow, R.; Drechsel-Grau, E.; Eichel, W.; Luthé, H.; Matter, Y. M.; Michaelis, W.; Boldt, P. *J. Org. Chem.* **1987**, *52*, 205. (i) Reference 2d. (j) Baban, J. A.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. II* **1981**, 161. (k) Salikhov, A.; Fischer, H. submitted for publication.
 (4) For recent theoretical studies on the addition of methyl and substituted methyl radicals to alkenes, see: (a) Zipse, H.; He, J.; Houk, K. N.; Giese, B. *J. Am. Chem. Soc.* **1991**, *113*, 4324. (b) Houk, K. N.; Paddon-Row, M. N.; Spellmeyer, D. C.; Rondan, N. G.; Nagase, S. *J. Org. Chem.* **1986**, *51*, 2874. (c) Fueno, T.; Kamachi, M. *Macromolecules* **1988**, *21*, 908. (d) Gonzales, C.; Sosa, C.; Schlegel, H. B. *J. Phys. Chem.* **1989**, *93*, 2435, 8388. (e) Arnaud, R.; Vidal, S. *New J. Chem.* **1992**, *16*, 471. (f) Tozer, D. J.; Andrews, J. S.; Amos, R. D.; Handy, N. C. *Chem. Phys. Lett.* **1992**, *199*, 229. (g) Arnaud, R.; Subra, R.; Barone, V.; Lelj, F.; Olivella, S.; Sole, A.; Russo, N. *J. Chem. Soc., Perkin Trans. II* **1986**, 1517. (h) Clark, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1774. (i) Arnaud, R. *New J. Chem.* **1989**, *13*, 543. (j) Reference 5.

In the present paper, we extend our earlier work by studying the reaction of *tert*-butyl radical with a set of monosubstituted alkenes, $\text{CH}_2=\text{CHX}$:



where X = H, NH_2 , F, Cl, CHO, and CN. Experimental results for the *tert*-butyl radical^{2a,3aj} present a somewhat confusing picture. On the one hand, the *tert*-butyl radical has been classified as strongly nucleophilic, based on the observation that the *tert*-butyl radical is significantly more reactive than the methyl radical in reactions with electrophilic alkenes.^{2a,3j} Consistent with this classification, Fischer has noted that activation energies for the addition of *tert*-butyl radical to a set of alkenes correlate with the alkene electron affinities.^{3a} Furthermore, Fischer also found that the *tert*-butyl addition reaction exhibits a large solvent effect, consistent with substantial charge transfer in the transition state.^{3k}

On the other hand, the activation energies for the addition of the series of alkyl radicals CH_3^\bullet , $\text{CH}_3\text{CH}_2^\bullet$, $(\text{CH}_3)_2\text{CH}^\bullet$, and $(\text{CH}_3)_3\text{C}^\bullet$ to ethylene are reported^{3a} as only varying slightly (from 32.2 kJ mol⁻¹ for CH_3^\bullet down to 27.6–29.6 kJ mol⁻¹ for $(\text{CH}_3)_3\text{C}^\bullet$). From a consideration of polar effects, it might have been anticipated that the nucleophilic *tert*-butyl radical would exhibit significantly lower barriers than the nonpolar methyl radical, even for addition to ethylene. The unexpectedly narrow range of observed barriers was rationalized in terms of superimposed steric interactions for the *tert*-butyl radical (which would tend to increase its barriers) and a SOMO–HOMO stabilizing interaction for methyl (which would tend to decrease its barriers).^{3a}

In the light of the above, we have undertaken a theoretical study of the addition reactions of the *tert*-butyl radical. It was hoped in the first place that such a study would help clarify the relative importance of enthalpy, polar, and steric factors for reactions of this radical with alkenes, ranging from electron rich to electron poor. Secondly, it was hoped to test the generality of the TS structure–enthalpy correlation for radical addition reactions that we found in our earlier work.^{5c} The curve-crossing model predicts that as the ionization energy of the radical is lowered, the charge-transfer contribution to the TS wave function will become increasingly important, and at some stage deviations from the TS structure–enthalpy correlation may occur. The *tert*-butyl radical, possessing a particularly low ionization energy, would be a suitable candidate to test the possible limits of the previously observed TS structure–enthalpy correlation.

Computational Procedures and Results

High-level ab initio calculations⁷ were carried out using the GAUSSIAN 92 series of programs⁸ for the reactants, products, and transition structures of reactions shown in eq 2 with X = H, NH_2 , F, Cl, CHO, and CN. Geometries were optimized and vibrational frequencies determined at the UHF/6-31G* level. Reaction barriers and enthalpies were then obtained using the quadratic configuration interaction procedure, QCISD,⁹ using the additivity approximation:

(7) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(8) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*; Gaussian Inc.: Pittsburgh, PA, 1992.

(9) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

$$\Delta E(\text{QCISD}/6-311\text{G}^{**}) \approx \Delta E(\text{QCISD}/6-31\text{G}^*) + \Delta E(\text{RMP2}/6-311\text{G}^{**}) - \Delta E(\text{RMP2}/6-31\text{G}^*) \quad (3)$$

Restricted open-shell second-order Møller–Plesset (RMP2) calculations¹⁰ were employed within the additivity scheme. Zero-point vibrational energies (ZPVEs) were obtained from the HF/6-31G* vibrational frequencies, scaled by a factor of 0.8929. Unless otherwise noted, the barriers and enthalpies referred to in the text correspond to such QCISD/6-311G**//UHF/6-31G* + ZPVE values. This represents the highest level of theory applied to date to study these reactions and is based on a recent assessment¹¹ of the performance of a variety of theoretical procedures in describing radical addition reactions. The choice of UHF/6-31G* for geometry optimization, in particular, is based on the finding for a small number of test systems that, in cases where spin contamination is significant, UHF geometries lead to higher-level relative energies closer to those obtained with QCISD(T) optimized structure than do UMP geometries. It is not practical to employ the QCISD(T) procedure for geometry optimizations in systems of the size examined in the present paper.

The extent of charge transfer between the radical and the alkene in the transition state was calculated at the HF/6-31G* level using both the Mulliken and the Bader¹² methods, with the latter employing the PROAIM program.¹³ Adiabatic ionization energies (*I*) and electron affinities (*A*) for *tert*-butyl radical were obtained at the G2(MP2) level of theory.¹⁴ This corresponds effectively to calculations at the QCISD(T)/6-311+G-(3df,2p) level, together with zero-point vibrational and isogyric corrections.

Calculated total energies are presented in Table 1, while corresponding optimized geometries are available as supplementary material in the form of printed archive files.¹⁵ Barrier heights and reaction enthalpies, together with ionization energy and electron affinity data for *tert*-butyl radical and the set of alkenes, are listed in Table 2. Structural and charge data for the transition states for *tert*-butyl radical attack on the set of alkenes are listed in Table 3. The more important geometrical parameters for the reaction transition state are defined in Figure 1.

Discussion

The Curve-Crossing Model. The manner in which the curve-crossing model may be used to build up the reaction profile for a radical addition reaction has been described in some detail in our earlier publications.^{5,16} The key point is that four valence-bond (VB) configurations may contribute to the ground-state wave function: DA, D³A*, D⁺A⁻, and D⁻A⁺. These are depicted in Chart 1. We use the Mulliken DA (donor–acceptor) terminology and arbitrarily denote the radical as D and the alkene as A. Thus, DA is the reactant configuration, D⁺A⁻

(10) Knowles, P. J.; Andrews, J. S.; Amos, R. D.; Handy, N. C.; Pople, J. A. *Chem. Phys. Lett.* **1991**, *186*, 130.

(11) Wong, M. W.; Radom, L. To be submitted for publication.

(12) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford Press: New York, 1990.

(13) Biegler-Konig, F. W.; Bader, R. F. W.; Tang, T.-H. *J. Comput. Chem.* **1982**, *3*, 317.

(14) (a) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **199**, *98*, 1293. (b) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(15) The optimized geometries are given as Z-matrices and summarized in the form of Gaussian archive entries.

(16) For previous applications of the curve-crossing model to radical reactions, see: (a) Shaik, S. S.; Bar, R. *Nouv. J. Chim.* **1984**, *8*, 11. (b) Shaik, S. S.; Hiberty, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 3089. (c) Pross, A. *Isr. J. Chem.* **1985**, *26*, 390. (d) Shaik, S. S.; Hiberty, P. C.; Lefour, J. M.; Ohanessian, G. *J. Am. Chem. Soc.* **1987**, *109*, 363. (e) Shaik, S. S.; Canadell, E. *J. Am. Chem. Soc.* **1990**, *112*, 1446.

Table 1. Calculated Total Energies^a (Hartrees), Zero-Point Vibrational Energies^b (ZPVE, kJ mol⁻¹), and S² Values^b Related to C(CH₃)₃[•] Addition Reactions to CH₂=CHX

	total energy				ZPVE	S ²
	HF/6-31G*	RMP2/6-31G*	RMP2/6-311G**	QCISD/6-31G*		
C(CH ₃) ₃ [•]	-156.675 01	-157.176 64	-157.301 98	-157.233 53	328.8	0.76
	Radical					
	Alkenes (CH ₂ =CHX)					
X = F	-176.881 95	-177.302 12	-177.415 65	-177.327 37	125.1	0.00
H	-78.031 72	-78.284 34	-78.343 58	-78.312 38	143.8	0.00
NH ₂	-133.061 96	-133.477 24	-133.570 88	-133.510 08	194.9	0.00
Cl	-536.933 69	-537.315 73	-537.399 38	-537.350 03	121.2	0.00
CHO	-190.762 42	-191.308 49	-191.416 65	-191.340 36	174.5	0.00
CN	-169.768 02	-170.292 72	-170.374 47	-170.319 66	144.3	0.00
	Transition Structures for C(CH ₃) ₃ [•] + CH ₂ =CHX					
X = F	-333.537 93	-334.470 78	-334.712 55	-334.550 68	456.5	1.02
H	-234.688 83	-235.453 14	-235.641 34	-235.535 41	476.3	1.02
NH ₂	-289.716 02	-290.647 32	-290.870 05	-290.734 17	527.1	1.01
Cl	-693.592 40	-694.487 36	-694.700 05	-694.575 71	453.0	1.02
CHO	-347.427 27	-348.485 63	-348.720 96	-348.570 27	505.2	1.17
CH	-326.433 60	-327.470 62	-327.679 99	-327.550 58	474.2	1.14
	Products [(CH ₃) ₃ CCH ₂ CHX [•]]					
X = F	-333.585 29	-334.523 03	-334.763 42	-334.599 30	471.1	0.76
H	-234.734 39	-235.503 44	-235.690 25	-235.581 66	485.9	0.76
Cl	-693.640 10	-694.538 81	-694.750 28	-694.624 20	465.7	0.76
NH ₂	-289.763 11	-290.699 33	-290.920 78	-290.783 52	541.1	0.76
CHO	-347.478 97	-348.541 17	-348.775 55	-348.624 18	518.7	0.91
CN	-326.484 59	-327.526 25	-327.734 71	-327.603 67	486.0	0.92

^a Based on UHF/6-31G* geometries ^b HF/6-31G* values.

Table 2. Calculated Barriers, Enthalpies, Ionization Energies (*I*), Electron Affinities (*A*), and Energies of Charge-Transfer States (D⁺A⁻ and D⁻A⁺) Related to C(CH₃)₃[•] Addition Reactions to CH₂=CHX

X	barrier ^a	enthalpy ^a	<i>I</i> ^{b,c}	<i>A</i> ^{b,c}	D ⁺ A ⁻ ^d	D ⁻ A ⁺ ^d
F	21.6	-89.5	10.37	-1.62	8.40	10.36
H	21.4	-87.8	10.58	-1.86	8.64	10.57
NH ₂	17.9	-95.7	8.18	-1.92	8.70	8.17
Cl	13.6	-99.1	9.98		8.06 ^e	9.97
CHO	6.5	-120.5	10.21	0.03	6.75	10.20
CN	1.9	-124.5	10.98	-0.23	7.01	10.97

^a QCISD/6-311G**+ZPVE values, in kJ mol⁻¹ (see text). ^b G2(MP2) adiabatic ionization energies (*I*) and electron affinities (*A*) of alkenes, in eV. ^c G2(MP2) (experimental in parentheses) *I* and *A* values for C(CH₃)₃[•] are 6.78 (6.70) and 0.01 eV, respectively. ^d Charge-transfer energies of separated reactants, calculated from theoretical *I* and *A* values for C(CH₃)₃[•] and CH₂=CHX. ^e Calculated using experimental electron affinity for chloroethylene (-1.28 eV), from: Jordan, K. D.; Burrow, P. D. *Chem. Rev.* **1987**, *87*, 557.

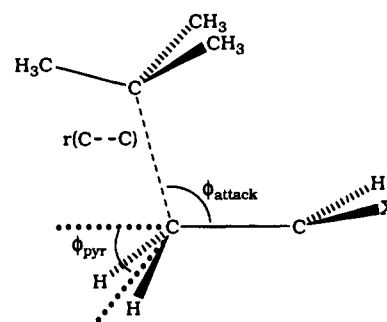
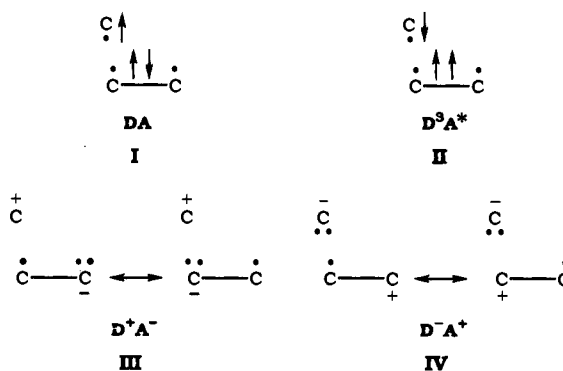
Table 3. Calculated Structural and Charge-Transfer Data Related to C(CH₃)₃[•] Addition Reactions to CH₂=CHX

X	charge transfer ^a		structural parameter ^b		
	Bader	Mulliken	r(C-C) ^c	φ _{attack} ^d	φ _{pyr} ^e
F	0.035	0.029	2.207	112.1	28.2
H	0.012	0.023	2.200	111.6	25.7
NH ₂	0.005	0.010	2.207	113.1	28.8
Cl	0.043	0.044	2.215	113.0	27.2
CHO	0.050	0.053	2.265	110.3	22.4
CN	0.051	0.059	2.267	110.7	22.5

^a Amount of charge transfer (CT) from the *tert*-butyl radical to the alkene in the transition structure (UHF/6-31G*). A positive value indicates electron transfer from the radical to the alkene. ^b UHF/6-31G* values. ^c Length (Å) of the forming bond between the *tert*-butyl radical and the alkene in the transition structure (see Figure 1). ^d Angle of attack (deg) of the *tert*-butyl radical in the transition structure (see Figure 1). ^e Extent of pyramidalization (deg) at the proximal alkene carbon in the transition structure (see Figure 1).

and D⁻A⁺ are the two possible charge-transfer configurations, and D³A* is the product configuration. The symbol ³A* in D³A* signifies excitation of the alkene to its π triplet state.

A configuration-mixing diagram, which enables the ground-

**Figure 1.** Schematic representation of the transition state for addition of *tert*-butyl radical to substituted alkenes.**Chart 1**

state reaction profile for addition of *tert*-butyl radical to an alkene to be built up from the basis set of configurations, is shown schematically in Figure 2. For simplicity, it is assumed that just one charge-transfer configuration, D⁺A⁻ (found to be the dominant one), is involved. The curves are drawn to correspond approximately to the energies (where available) for addition to the parent ethylene. The reactant configuration (DA) rises in energy as the reaction proceeds because repulsive interactions set in between the odd electron on the radical and the two π electrons. The product configuration, D³A*, initially high in energy since the π bond has been excited to the triplet

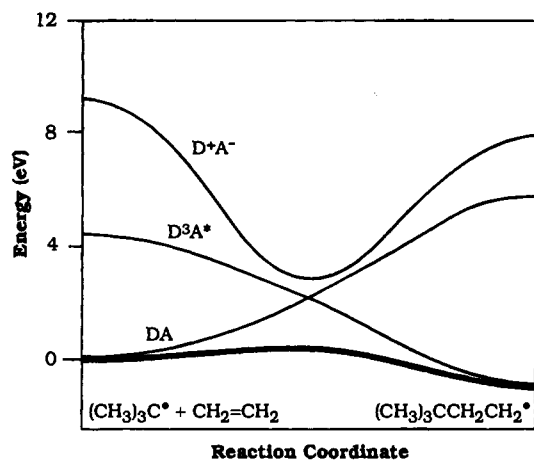


Figure 2. Curve-crossing diagram showing the mixing of DA, D^3A^* , and D^+A^- configurations in the schematic generation of the ground-state reaction surface (bold line) for the addition of *tert*-butyl radical to monosubstituted ethylenes. The curves are drawn to correspond approximately to the energies (where available) for the system of *tert*-butyl radical plus ethylene.

configuration, drops in energy along the reaction coordinate, since the odd electron on the radical can now pair up with an uncoupled electron in the π system to form a C–C bond. The initial energy of D^3A^* is estimated¹⁷ to be in the range 3.8–4.5 eV.

The initial energy of the D^+A^- configuration for the system of *tert*-butyl and a family of substituted ethylenes lies in the range 7.0–8.7 eV relative to DA, based on the calculated ionization energies and electron affinities listed in Table 2. However, due to the electrostatic attraction between positive and negative moieties, it is likely to drop sharply in energy as reactants approach one another (simple electrostatic considerations suggest the drop will be ca. 6 eV^{3a,5b}), so for this system the energy of D^+A^- in the transition state region would appear to lie very close to that of the crossing point of DA and D^3A^* . This situation is in marked contrast to the previously studied reactions of the methyl radical where the charge-transfer configurations were generally found to lie substantially above the crossing point. Accordingly, we may expect that the charge-transfer configuration will play a significantly more important role in the addition reactions of the *tert*-butyl radical.

The ground-state energy profile for the reaction of *tert*-butyl radical with substituted alkenes, shown schematically as a bold line in Figure 2, can be described by the wave function Ψ_G , which is a resonance mixture of the reactant, product, and charge-transfer configurations

$$\Psi_G: \quad DA \leftrightarrow D^3A^* \leftrightarrow D^+A^- \quad (4)$$

Based on a recent theoretical study by Shaik et al.,¹⁹ an approximate description of the transition state may be formally given by the wave function

$$\Psi_{TS} = N\{2^{-1/2}[DA + D^3A^*] + \lambda[D^+A^-]\} \quad (5)$$

where λ is the D^+A^- mixing parameter. Such a description of the transition state assumes that the transition state is in the

(17) The G2(MP2) vertical triplet excitation energy of ethylene is 434 kJ mol⁻¹ (4.50 eV) (experimental¹⁸ 4.3 eV) and substituents tend to reduce this value (e.g. the calculated value for cyanoethylene is 374 kJ mol⁻¹ (3.88 eV)).

(18) Flicker, W. M.; Mosher, O. A.; Kupperman, A. *Chem. Phys. Lett.* **1975**, *36*, 56.

(19) Shaik, S.; Ioffe, A.; Reddy, A. C.; Pross, A. *J. Am. Chem. Soc.* **1994**, *116*, 262.

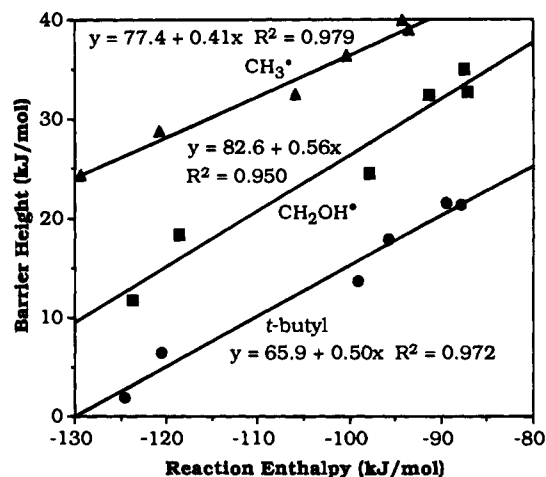


Figure 3. Plot of barrier height against reaction enthalpy (QCISD/6-311G** + ZPVE, kJ mol⁻¹) for the addition of CH_3^* (\blacktriangle), CH_2OH^* (\blacksquare), and *tert*-butyl (\bullet) radicals to alkenes $CH_2=CHX$ ($X = H, NH_2, F, Cl, CHO, \text{ and } CN$).

immediate vicinity of the crossing point of reactant and product configurations. This assumption was found to hold well over a wide range of transition state structures in the initial study.¹⁹ In the case of the addition reactions of *tert*-butyl radical, however, the D^+A^- configuration has a particularly low energy, as noted above. It is of interest to see whether the increasing D^+A^- contribution has structural consequences for the transition states for such reactions.

Analysis of the *ab Initio* Data. The three main factors that are thought to affect the barrier height for radical addition to alkenes are (a) reaction enthalpy, (b) the degree of charge-transfer character in the transition state, and (c) steric repulsion in the transition state. A first step in assessing the relative importance of these factors for the addition of *tert*-butyl radical to the set of alkenes, $CH_2=CHX$, is to plot the dependence of barrier height on the enthalpy of reaction, using the results presented in Table 2. This is shown in Figure 3, together with plots for the previously studied CH_3^* and CH_2OH^* radicals.

The plot of barrier height versus reaction enthalpy for *tert*-butyl radical addition gives a good correlation ($R^2 = 0.972$), as observed previously for CH_3^* and CH_2OH^* . This suggests that, as for these other radicals, enthalpy is a key factor in determining the barrier height. The more exothermic the reactions, the lower the barrier height is, in accordance with the generalized Bell–Evans–Polanyi relationship²⁰ (equivalent to a rate–equilibrium relationship) that links these two parameters. An increase in reaction exothermicity of 35 kJ mol⁻¹ leads to a reduction in barrier height of ca. 20 kJ mol⁻¹.

The importance of polar effects may be tested in principle by plotting the barrier height for radical addition against alkene electron affinity. Such a plot for the *tert*-butyl radical shows a reasonable correlation ($R^2 = 0.854$). However, the significance of this result is not clear, given the fact that electron affinity and reaction enthalpy for radical additions are themselves correlated. This complication has been discussed in detail in our earlier work.⁵

Information regarding the polar character of the transition state may be obtained from the calculated energy and charge data. In the first place, charge-transfer energies may be obtained from the *I* and *A* data for the radical and substrate and these indicate (Table 2) that for most alkene substrates the energy of the D^+A^- configuration is substantially lower than that of the

(20) (a) Bell, R. P. *Proc. R. Soc. London Ser. A* **1936**, *154*, 414. (b) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1936**, *32*, 1340.

corresponding D^+A^- configuration. These data suggest that the *tert*-butyl radical is *nucleophilic* in character. It is only for $CH_2=CHNH_2$ that D^+A^- is the lower energy configuration, but the significance of the D^+A^- value in this case is not certain.²¹ The calculated charges in the transition state for the addition reactions (Table 3) are supportive of this general picture, indicating that *tert*-butyl radical is an electron donor in all cases.

In order to assess the *energetic* consequences of the charge-transfer contributions, we need to compare the *tert*-butyl correlation line with the earlier data for CH_3^* and CH_2OH^* , as shown in Figure 3. In our previous study,^{5c} we explained the lower energy of the CH_2OH^* correlation line compared with the CH_3^* line, by invoking a polar contribution to the transition state for CH_2OH^* addition, associated with the mixing in of D^+A^- into the transition state wave function. The ionization energy of the CH_2OH^* radical (7.43 eV) is lower than that for CH_3^* (9.77), so the D^+A^- energies for CH_2OH^* addition are lower than for CH_3^* addition, leading to enhanced polar character and a reduced energy barrier. As a result, the CH_2OH^* barrier height correlation line is displaced to lower energy compared with that for CH_3^* . Indeed *the gap between the CH_3^* and CH_2OH^* lines was considered to provide a rough estimate of the polar stabilization for the CH_2OH^* transition state at a given reaction enthalpy.*

Inspection of Figure 3 shows that the *tert*-butyl correlation line lies well below both the CH_3^* and the CH_2OH^* correlation lines. Again, by assuming that the energy gap between the correlation lines provides a measure of the polar stabilization in the transition state, we may conclude that the energetic effect of the polar contribution for the *tert*-butyl radical is about 20–25 kJ mol⁻¹ compared with the CH_3^* reference, significantly larger than for the CH_2OH^* radical (5–15 kJ mol⁻¹). The larger polar stabilization for *tert*-butyl compared with CH_2OH^* may be readily attributed to the lower ionization energy of the *tert*-butyl radical (6.78 eV) compared with the CH_2OH^* radical (7.43 eV). Consequently, the lower energies of the D^+A^- configurations for the *tert*-butyl radical lead to greater D^+A^- mixing, greater polar character in the *tert*-butyl transition states, and correspondingly lower barriers. Indeed, for the electron-withdrawing substituents in the alkene, CHO and CN, where the energy of D^+A^- for *tert*-butyl radical drops to 6.75 and 7.01 eV, respectively, the barrier almost entirely disappears (down to just 6.5 and 1.9 kJ mol⁻¹, respectively). Consistent with this interpretation, Bader charges on the radical in *tert*-butyl transition states (Table 3) are larger than the corresponding values previously found in CH_2OH^* transition states,^{5c} confirming that there is more charge transfer in the *tert*-butyl reactions than in the CH_2OH^* reactions. We conclude, therefore, that in the gas phase, the *tert*-butyl radical is more nucleophilic and hence more reactive than CH_2OH^* in its addition reaction to alkenes.

One point that appears initially surprising is the fact that the polar stabilization energies for the electrophilic alkenes ($CH_2=CHCN$ and $CH_2=CHCHO$) are similar to those for the other alkenes studied. This result contrasts with that for the less nucleophilic radical CH_2OH^* , where a trend toward increasing polar stabilization with the more electrophilic alkenes was found (reflected in the slope of the CH_2OH^* line being greater than that of the CH_3^* line), as would be expected.^{3c} It should be noted, however, that for *tert*-butyl addition to $CH_2=CHCN$ and $CH_2=CHCHO$, the barrier has almost entirely disappeared

(being just 1.9 kJ mol⁻¹ for $CH_2=CHCN$). As the energy of D^+A^- is lowered by increasingly electron-withdrawing groups, the barrier height is expected to drop away toward zero. Some barrier to reaction is expected to remain, however, since initially, when the reactants are infinitely separated, the energy of D^+A^- is relatively high and unlikely to contribute significantly to the overall wave function. Hence, the reaction profile is *initially dictated by the reactant configuration which increases in energy along the reaction coordinate* leading to the expectation of a barrier, even for strongly electron-withdrawing groups. In summary, the observation that polar stabilization energies in the transition states for the reactions of *tert*-butyl radical with electrophilic alkenes are not greater than those for the other alkenes may be accounted for by noting that the barrier is unlikely to disappear, thus limiting the extent of any transition state stabilization.

Several of our results suggest that steric factors do not significantly influence the barrier heights for *tert*-butyl addition, at least for the alkenes examined in the present study. In the first place, the transition state C—C bond in these reactions is long (ca. 2.2 Å, Table 3), making strong interaction between radical and substrate unlikely. Second, the barrier heights for *tert*-butyl radical addition vary linearly with the enthalpy changes for the addition reaction, as found also for methyl (Figure 3). If steric interactions played a significant role in the addition reactions of *tert*-butyl radical, then some departures from the smooth correlation might have been expected. Next, we find that the energy required to bend the methyl and *tert*-butyl radicals to the same extent as in their respective transition structures for addition to ethylene is quite similar: 6.7 and 6.1 kJ mol⁻¹, respectively (RMP2/6-31G**//UHF/6-31G*). Again, if steric effects were important, we would have expected the *tert*-butyl value to be considerably larger. Finally, for a given enthalpy change, the barrier heights for *tert*-butyl radical addition are all lower than for methyl addition. While polar effects should indeed lower the barrier, as noted above, steric interactions would have been expected to increase the barriers.

We note that while the theoretical data indicate that the barrier for *tert*-butyl addition to ethylene is substantially less than that for methyl addition (21.4 kJ mol⁻¹ for *tert*-butyl compared with 38.9 kJ mol⁻¹ for methyl), experimental gas-phase data place these barriers much closer together (28.8 kJ mol⁻¹ for *tert*-butyl compared with 34.8 kJ mol⁻¹ for methyl).²² We are unable to explain this apparent discrepancy.²³

Scope of the TS Structure—Enthalpy Correlation. In our earlier paper,^{5c} we reported a correlation between TS structure and reaction enthalpy for the addition reactions of the radicals CH_3^* , CH_2OH^* , and CH_2CN^* to the family of alkenes $CH_2=CHX$, and this correlation was rationalized with the aid of the curve-crossing model. According to the model, the *structure* of the transition state is determined primarily by the crossing point of DA and D^3A^* configurations. Since the energy of D^3A^* governs the reaction enthalpy, a correlation between TS structure and reaction enthalpy is observed, in which more exothermic reactions tend to have “earlier” or looser transition states.^{5c} It appears that in these cases the mixing in of a third configuration does not appear to significantly influence the *position* of the

(22) Kerr, J. A. In *Free Radicals*; Kochi, J., Ed.; Wiley: New York, 1972; Vol. 1. The experimental barriers are 29.7 kJ mol⁻¹ at 415 K for *tert*-butyl addition and 33.1 kJ mol⁻¹ at 403 K for methyl radical addition to ethylene which, when corrected to 0 K using our calculated vibrational frequencies, become 28.8 and 34.8 kJ mol⁻¹, respectively.

(23) In order to provide a check on our prediction that the barrier for *tert*-butyl addition to ethylene is significantly less than that for methyl addition, we have calculated the barriers at the QCISD(T)/6-311G** level (obtained via an additivity relationship directly analogous to eq 3). At this (higher) level of theory, we find that the barrier difference widens slightly further to 20.7 kJ mol⁻¹.

(21) The situation for $CH_2=CHNH_2$ is complicated by the fact that ionization removes an electron associated to a significant extent with the nitrogen lone pair (rather than just the ethylenic double bond) and so the appropriateness of the calculated ionization energy in the evaluation of the D^+A^- energy is not entirely clear.

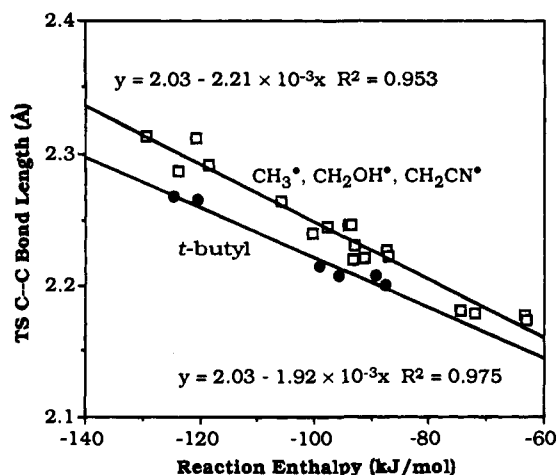


Figure 4. Plot of C--C bond length in the transition state (UHF/6-31G*, Å) against reaction enthalpy (QCISD/6-311G* + ZPVE, kJ mol⁻¹) for the addition of CH₃[•], CH₂OH[•], and CH₂CN[•] (□) and *tert*-butyl (●) radicals to alkenes CH₂=CHX (X = H, NH₂, F, Cl, CHO, and CN).

transition state, though it is found to have a significant effect on the *energy* of the transition state, consistent with the recent proposal by Shaik et al.¹⁹

We pointed out, however, that in cases where the charge-transfer configuration is strongly stabilized, some deviation from the TS structure–reaction enthalpy correlation might be anticipated. It seems likely that as the charge-transfer configuration becomes lower in energy, a point will be reached where not only the energy of the transition state but also its structure will be significantly affected. When this point is reached, the structure of the transition state and the crossing point of DA and D³A* may increasingly diverge, and the observed correlation between transition state structure and reaction enthalpy will deteriorate. It was therefore of interest to see whether the highly nucleophilic *tert*-butyl radical, with a large D⁺A⁻ contribution to the transition state, would conform to the TS structure–enthalpy plot observed for the CH₃[•], CH₂OH[•], and CH₂CN[•] set of radicals.

A TS structure–enthalpy plot for the set of four radicals CH₃[•], CH₂OH[•], CH₂CN[•], and *tert*-butyl is shown in Figure 4. When all four radicals are included, a reasonable (though not outstanding) correlation is found ($R^2 = 0.869$). Thus it would appear that the TS structure–enthalpy correlation holds to a reasonable extent, even for a highly nucleophilic radical. Closer inspection of Figure 4, however, reveals that removal of the *tert*-butyl points significantly improves the correlation for the other three radicals ($R^2 = 0.953$). The points for *tert*-butyl, when correlated separately ($R^2 = 0.975$), tend to lie on a line representing a somewhat *tighter* TS structure than that expected on the basis of the TS structure–enthalpy correlation derived from the less polar radicals. Thus, our results suggest that as the degree of charge transfer in the transition state becomes substantial, the

electrostatic attraction between the oppositely charged moieties in the transition state not only stabilizes it but also influences its structure. The consequence is a *decrease* in the incipient C--C bond length in the transition state. Although, on present evidence, the general nature of the TS structure–enthalpy correlation appears to hold up quite well, our results show a small deviation for the *tert*-butyl radical and suggest that radicals with more pronounced polar character in the TS than *tert*-butyl will show still larger deviations.

Conclusions

This theoretical study of the addition reaction of *tert*-butyl radical to alkenes leads to the following conclusions.

(1) The reactivity of the *tert*-butyl radical in the gas phase depends on a combination of enthalpy and polar effects. The magnitude of polar stabilization of the transition state (due to D⁺A⁻ mixing) appears to be ca. 20–25 kJ mol⁻¹. An enthalpy variation of 35 kJ mol⁻¹ leads to a change in barrier height of ca. 20 kJ mol⁻¹.

(2) Barrier heights for *tert*-butyl addition to alkenes are found to be substantially lower than for the corresponding CH₃[•] addition reaction (by 20–25 kJ mol⁻¹) due to the strong nucleophilic character of the *tert*-butyl radical. The relatively low barrier heights for *tert*-butyl addition are found to apply to the entire set of alkenes and not just the electrophilic alkenes.

(3) The *tert*-butyl radical is found to be more nucleophilic and, therefore, more reactive than the CH₂OH[•] radical, and this is attributed to the lower ionization energy of *tert*-butyl radical compared with CH₂OH[•].

(4) Our previous observation of a general transition state structure–enthalpy correlation for the radicals CH₃[•], CH₂OH[•], and CH₂CN[•] is maintained, albeit with a slightly poorer fit, when the *tert*-butyl radical is added to the set. The points for the *tert*-butyl radical when considered separately are found to be slightly displaced from the correlation line for CH₃[•], CH₂OH[•], and CH₂CN[•]. This small displacement reflects a slightly tighter transition state for *tert*-butyl reactions, which may in turn be attributed to a larger contribution of the charge-transfer configuration, D⁺A⁻.

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Supplementary Material Available: Listing of geometries optimized at the UHF/6-31G* level for the species involved in the addition of *tert*-butyl radical to the CH₂=CHX alkenes (X = H, NH₂, F, Cl, CHO, and CN) (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.