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# Transition State Energy Stabilization in the Reactions Allyl + Propene and Methyl + 1,3-Butadiene

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Abstract: Critical energies  $(E_0)$  for reactions involving resonance stabilized reactants and/or products were measured by studying the  $\beta$  scission decomposition of chemically activated alkyl and alkenyl radicals. For the reverse process, addition of a radical to a double bond was obtained by microscopic reversibility. For these  $\beta$  scission decompositions, 67% of the TS stabilization energy is obtained from the reactants and the remaining 33% from the products. It was found that the reaction allyl + propene has a critical energy,  $E_0$ , approximately  $6.8 \pm 0.3$  kcal/mol greater than that for the reaction propyl + propene. The critical energy for the anti-Markovnikov addition of methyl to 1-butene relative to that for the Markovnikov addition is discussed.

The question has often been asked as to the amount of stabilization which occurs in the transition state (TS) for reactions involving either resonance stabilized reactants or products. The inherent energy stabilization can only be measured in the gas phase where solvent perturbations are absent since solvent stabilization energies in solution may or may not be equal in the reactant and transition states. Energy stabilization of either the reactant or the TS will directly affect the critical energy of the reaction  $(E_0)$  which in turn appears in the temperature dependence of the rate constant, i.e., the experimentally observed activation energy. For a given reaction, energy stabilization of reactants will increase the observed activation energy while if only the TS is stabilized the observed activation energy will decrease. The absolute amount of stabilization in either reactant or TS can be obtained by measuring the difference in critical energy of two analogous reactions, one of which involves stabilization in either the reactant or product state.

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The absolute amount of TS stabilization will depend on whether the TS is best characterized by the reactant or product state. Thus the position of the TS on the reaction coordinate and the contribution of stabilization from reactants and products can be determined from relevant activation or critical energy measurements. In this work the unimolecular decomposition of chemically activated radicals (R\*), produced by the addition of thermalized hydrogen atoms to an olefin (Ol), results in the production of two fragments: a smaller radical (R') and olefin (Ol').

$$H + Ol \longrightarrow R^* \longrightarrow R' + Ol' + \Delta E$$

Rate constants relative to a standard reaction [the decomposition of 2-methylbutyl-2 (2MB2)] were measured. The observed unimolecular rate constant,  $k_a$ , is related to the following fundamental quantities: the energy of excitation, the vibrational frequency pattern of the radical and decomposition TS, and the critical energy for the reaction, by the quantum statistical formulation of unimolecular reactions developed by Marcus and Rice<sup>1</sup> (RRKM). The first three

Tardy / Reactions of Allyl + Propene and Methyl + 1,3-Butadiene

The validity of the RRKM models as applied to unimolecular processes has been supported by numerous experimental studies;<sup>2-5</sup> the work by Rabinovitch and coworkers<sup>2-4</sup> has been particularly useful. Experiments designed to give the dependence of the decomposition rate constant on the excitation energy of the butyl-2<sup>2</sup> radical support the RRKM predictions. Studies involving the carbon-carbon bond rupture in a homologous series of vibrationally excited alkyl radicals have given insight into the frequency patterns of the activated complex.<sup>3,4</sup> Thus with the available evidence<sup>2-5</sup> supporting the RRKM model, one can use this model to provide information on the critical energy for a reaction if the rate constant, excitation energy, and vibrational frequency assignments are known.

## **Experimental Section**

1-Hexene (1H), 2-methyl-1-butene (2M1B), and 1,5-hexadiene (15H) purchased from Chemical Samples Co. were purified by preparative GLC. A 30 to 1 mixture of hydrogen and olefins was made by adding tank hydrogen passed through a silica gel packed U tube held at -195° to an olefin mixture (1H and 2M1B or 15H and 2M1B) in a 12 l. Pyrex storage vessel. Pressures were measured by either a Barocel membrane manometer  $(10^{-4} \text{ to } 10 \text{ Torr})$ , mercury manometer (1 to 760 Torr), or a Bourdon Gauge (500 to 10<sup>4</sup> Torr). An aliquot of the above mixture was transferred to a 1 l. stainless steel cylindrical reaction vessel, which was fitted with a 22 mm o.d. thick wall quartz tube mounted along the axis of the reactor. A G8T5 germicidal lamp was placed in the quartz tube; approximately 90% of the radiation was blocked by an opaque filter. Tank hydrogen was then added such that the reaction mixture had a ratio of hydrogen to total olefin in excess of 200 to 1. The hydrogen atoms were produced, in situ, by the mercury photosensitization of molecular hydrogen at room temperature. Photolysis times ranged from 10 to 800 sec. After photolysis the reaction vessel was pumped through a packed U tube cooled to -195°. The condensable gases were then injected into a 20 ft hexamethylphosphoramide GC column at room temperature and analyzed with a flame ionization detector. Authentic samples were injected for peak identification purposes. Peak height times retention time corrected by carbon number was found to adequately represent the molar amount of compound present. None of the decomposition products were observed with runs performed in which the lamp remained off.

## **Experimental Results**

The pertinent reactions are

$$H_{2} + Hg({}^{3}P_{1}) \longrightarrow 2H + Hg({}^{1}S_{0})$$

$$H + 2M1B \stackrel{h'}{\longrightarrow} 2MB2^{*} \stackrel{k_{a}^{3}}{\longrightarrow} C_{4}H_{8}(D^{s}) + CH_{3}$$

$$\stackrel{\omega_{eff}}{\longrightarrow} C_{5}H_{11}(S^{s})$$

$$H + 1H \stackrel{h'}{\longrightarrow} H2^{*} \stackrel{k_{a}^{H2}}{\longrightarrow} C_{3}H_{8}(D) + C_{3}H_{7}$$

$$\stackrel{k_{1}}{\underset{k_{1}'}{\overset{\omega_{eff}}{\longrightarrow}}} isomers of H2$$

$$H + 15H \stackrel{h'}{\longrightarrow} 1H5^{*} \stackrel{k_{a}^{1H5}}{\longrightarrow} C_{3}H_{6}(D) + C_{3}H_{5}$$

$$\stackrel{k_{1}}{\underset{k_{1}'}{\overset{\omega_{eff}}{\longrightarrow}}} isomers of 1H5$$

$$\stackrel{\mu_{1}}{\underset{k_{1}'}{\overset{\omega_{eff}}{\longrightarrow}}} 1H5(S)$$

where  $\omega_{\text{eff}}$  is the effective collision frequency for stabilization, D and S are the decomposition and stabilization yields, respectively,  $k_a$  is the observed rate constant, and the s superscripts refer to the reaction of the internal standard, 2M1B.

The reactions were carried out at high pressures so that any reversible isomerization,<sup>6-8</sup> via hydrogen migration or internal addition (i.e., cyclization), can be quenched; this requires that  $\omega_{eff} > k_i$  or  $\omega_{eff} > 10^9 \text{ sec}^{-1}$ , i.e., pressures greater than 1 atm. With this provision, the steady state expression for the excited radical R\* (H2 or 1H5) is simplified and the system in fact reduces to a simple competitive decomposition system.<sup>9</sup> It has been shown previously that the rate constant at high pressure for a specific process is independent of the competing processes,<sup>9</sup> thus the observed rate constant,  $k_a$ , is defined in the conventional manner by  $k_a = \omega_{eff} D/S.^{10}$ 

The ratio S/D may be determined from an internal standard for which  $S^s/D^s$  is known by the equation<sup>11</sup>

$$\frac{S}{D} = \frac{x}{x^{s}} \frac{f}{f^{s}} \frac{D^{s}}{D} \left( \frac{S^{s}}{D^{s}} + 1 \right) - 1$$

where x is the mole fraction of olefin and f is the specific rate of hydrogen atom addition to olefin. At high pressures

$$\frac{k_{a\infty}}{k_{a\infty}} = \frac{\omega D/S}{\omega^s D^s/S^s} = \frac{\omega}{\omega^s} \frac{x^s f^s}{xf} \frac{D}{D^s}$$

Since the moderator gas in these experiments (hydrogen) is not an efficient deactivator,  $\omega$ , the actual number of collisions per second suffered by R\* may not be set equal to  $\omega^s$ . In principle, an inefficiency factor,  $\beta$ ,<sup>11-13</sup> must be used to relate  $\omega$  and  $\omega_{eff}$ ; however, it can be argued that the relative efficiency  $\beta/\beta^s$  which appears when calculating relative rate constants is approximately 1.<sup>11,14</sup> The calculations presented in this paper do not make this assumption, and in fact show that within 20% this assumption is valid. From simple collision theory the factor  $f/f^s$  is 1 for the H2 system and 2 for the 15H system.

The experimental values of  $k_a$  and  $k_a/k_a^s$  for the H2 and 1H5 system are shown in Table I along with the pertinent experimental data. The  $k_a$  value for the H2 system (1.8 × 10<sup>6</sup>) agrees with the previous results reported by Rabinovitch and coworkers (1.9 × 10<sup>6</sup>).<sup>3</sup> It is concluded from this work that  $k_{a\infty}^{\text{H5}}/k_{a\infty}^{\text{H2}}$  is 18.

## **Calculational Results**

For a strong collider the observed rate constant  $k_{a\infty}$  can be computed from fundamental quantities by the following equation<sup>9,10</sup>

$$k_{a\infty} = \int_{E_0}^{\infty} k_E f_E dE$$
$$f_E = k_E' B_E dE / \int_{E_0}^{\infty} k_E' B_E dE$$

where  $f_E$  is the normalized distribution function for the formed radical with internal energy E,  $k_E$  and  $k_E'$  are the microscopic rate constants for the C-C and C-H decomposition reactions, respectively, and  $B_E$  is the Boltzmann distribution of internal energy states for R\* at the temperature in question. The  $k_E$ 's are calculated from the RRKM expression:<sup>1</sup>

$$k_E = \frac{1}{h} \frac{\sum\limits_{E^*=0}^{E-E_0} P_{vr}(E^*)}{N_E^*}$$

Journal of the American Chemical Society / 97:20 / October 1, 1975

Table I. Summary of Experimental Results<sup>a</sup>

System	No. of runs <sup>a</sup>	$x/x_s$	$f/f_8$	$D/D^{s}$	$k_{a\infty}/k_{a\infty}^{s}$	$k_{a\infty}$ , sec <sup>-1</sup> b	$k_{a_{\infty}}$ 1H5/ $k_{a_{\infty}}$ H2
H + 1H → H2	6	0.898	1	$0.44 \pm 0.02$	0.49	1.8 × 10 <sup>6</sup>	
H + 15H → 1H5	5	1.044	2	$18.7 \pm 2.2$	8.95	$3.2 \times 10^{7}$	18

<sup>a</sup> All runs with total pressure in excess of 1 atm. <sup>b</sup> Assuming  $k_{ax}^{s} = 3.6 \times 10^{6}$  as given in ref 7.

Table II.	Summary	of Calculational	Results
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	E <sub>0</sub> , kcal/ mol	$\Delta E_{o},$ kcal/mol	$k_{a\infty}$ , sec -1		$k_{a\infty}^{1H5}/k_{a\infty}^{H2}$		$k_{a\infty}^{1H5(normal)/k_{a\infty}^{1H5(allyl)}}$		a = k (SC)/k
System (TS Model)			400 SL	SC	400 SL	SC	400 SL	SC	$k_{a\infty}(400 \text{ SL})$
$H + 1H \rightarrow H2$ ("normal")	31.1	0	2.45 × 10 <sup>6</sup>	5.37 × 10 <sup>5</sup>	-				0.219
$H + 15H \rightarrow 1H5$ ("normal")	31.1	0	$6.26 \times 10^{6}$	$1.38 \times 10^{6}$	2.55	2.57	1.45	1.45	0.220
	29.1	2	$3.38 \times 10^{7}$	$6.89 \times 10^{6}$	13.80	12.83	1.45	1.45	0.204
	27.1	4	$1.65 \times 10^{8}$	$3.12 \times 10^{7}$	67.53	58.15	1.45	1.45	0.188
	25.1	6	$7.5 \times 10^{8}$	$1.30 \times 10^{8}$	306.45	242.22	1.45	1.45	0.173
$H + 15H \rightarrow 1H5$ ("allyl")	31.1	0	$4.31 \times 10^{6}$	$9.52 \times 10^{5}$	1.76	1.77			0.221
	29.1	2	$2.34 \times 10^{7}$	$4.76 \times 10^{6}$	9.54	8.87			0.205
	27.1	4	$1.14 \times 10^{8}$	$2.16 \times 10^{7}$	46.59	40.20			0.189
	25.1	6	$5.18 \times 10^{8}$	9.00 × 10 <sup>7</sup>	211.60	167.60			0.174

Table III.	Frequency	Assignments for	the H2 and	1H5 Systems
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	No. of modes					
			15H system			
	H1	system		1H5 "iso-	TS	
Type of mode <sup>a</sup>	H2_	H2 TS	<u>1H5</u>	lated"	"allyl"	
C—H stretch [2950]	13	13	11	11	11	
C—C stretch [950]	5	3	4	2	1	
C==C stretch [1650]			1	1		
CC stretch [1350] <sup>b</sup>		1		1	1	
C—C stretch in C $\xrightarrow{\dots}$ C					1	
$[1300(2)]^{b}$						
CH <sub>3</sub> bends	2	2	1	1	1	
[1462 (2), 1374, 1168,						
950]						
$H_2C = bends [1440, 978, 0.00]$			1	1	1	
907 J				1	1	
= C - H bends [1300, 920]			I	1	T	
· C — H bends [1260, 768]	1	1	1	1	1	
CH, bends						
[1450, 1310, 1260, 768]	3	1	2			
[1450, 1310, 630, 768] <sup>b</sup>		2		2	2	
CCC bends [474, 370]	1	1	1	1	1	
[303, 139]	1		1			
[152, 69] <i>b</i>		1		1	1	
CC torsions						
[212 (2), 125, 94, 61]	1					
[212 (2), 108, 229 30] <sup>b</sup>		1				
[650, 212, 125, 94, 61]			1			
$[650, 212, 108, 229, 30]^{b}$				1		
[431, 212, 229, 229, 30] b					1	

a [1300 (2)] designates 2 frequencies of 1300 cm<sup>-1</sup>. b Designates modes which apply to TS.

where

$$\sum_{E^+=0}^{E^-E_0} P_{\rm vr} \, (E^+)$$

is the sum of vibration-rotation energy states of the TS up to the energy in question,  $N_E^*$  is the density of vibrationrotation energy states of the excited radical, and h is Planck's constant. Thus a knowledge of the vibrational frequency pattern and  $E_0$  is sufficient to calculate  $k_E$ .

For weak collisions  $k_{a\infty}$  must be calculated<sup>11</sup> from both the  $k_E$ 's and the collision transition probabilities for energy transfer. These probabilities for hydrogen have been discussed elsewhere<sup>11</sup> and are approximated by a model consisting of a single jump (up or down) of approximately 400  $cm^{-1}$  (commonly given the shorthand notation 400 SL). Thus for a known weak collider model, as for a strong collider model, only the frequency pattern and  $E_0$  are necessary.

Vibrational frequency models for radical and TS have been tested by Rabinovitch<sup>3</sup> for the analogous decomposition in the homologous series: butyl-2 through octyl-2. The preferred frequency model, due to simplicity and available frequency assignments, generates  $k_E$ 's which are too small by a factor of 2.2, consequently all calculated rates must be multiplied by this "calculational factor". However, it should be noted that the "calculational factors" for absolute rate constants cancel when relative rate constants are compared. This accepted frequency model also agrees with recent normal mode calculations.<sup>15</sup>

The calculated value of  $k_{a\infty}$  for H2 is shown in Table II along with the accepted values for  $E_0$  and the minimum energy of excitation,  $E_{min}$ . The "group" frequency assignments for H2, using the method developed by Larson and Rabinovitch,<sup>7</sup> are given in Table III; with these frequencies and the present calculational technique the calculational factor is 3.5.

The frequency assignment for the 1H5 radical can be obtained by deleting 2 C-H stretches and 4 C-H bends and replacing the CH<sub>3</sub>-C torsion by a CH<sub>2</sub>=C torsion and a C-C stretch by a C=C stretch. However, when assigning the TS of 1H5 two vibrational models must be considered depending upon the stabilization of the TS. First, the C=C can be considered isolated from the reaction coordinate. This model ("normal") corresponds to no delocalizations of the  $\pi$  electrons in the TS. The other model ("allyl") corresponds to partial delocalization; i.e., the TS corresponds to an allyl radical + propene. The "group" frequency assignments<sup>7</sup> for these models are listed in Table III. The rate constant for these two models differ by a factor of 1.45 as shown in Table II.

With both  $E_0$ 's set to 31.1 kcal/mol (the accepted value for H2 decomposition) and at low levels of excitation,  $E \sim E_0$ ,  $k_E^{1H5}$  will be greater than  $k_E^{H2}$  since the 1H5 radical is "tighter" than the H2 radical. This is due to the presence of the carbon-carbon double bond, which decreases the density of states for 1H5 compared to H2. When the  $k_E$ 's are averaged over the proper formation distribution function, a quantum statistical weight effect (QSWE) ( $k_{a\infty}^{1H5}/k_{a\infty}^{H2}$ ) of 2.57 and 1.77 is calculated for the "normal" and "allyl" models, respectively. This value, of course, is dependent upon  $E_0$ .

Calculational results for a strong (SC) and a weak colli-



Figure I. Reaction profiles for the H + 1-hexene (1H) and H + 1,5-hexadiene (15H) systems. For comparative purposes the zero point energy levels of the H2 and 1H5 radicals have been set equal to zero.

der (step ladder model with steps of 400 cm<sup>-1</sup>: 400 SL) are summarized in Table II. These results show that the collisional efficiency,  $\beta$ , as defined<sup>11</sup> by

$$\beta = k_{a\infty}(\text{strong})/k_{a\infty}(\text{weak})$$

has an insignificant dependence on the system or TS model and a slight dependence on  $E_0$ ; as  $E_0$  decreases by 6 kcal/ mol  $\beta$  decreases by ~22%.

In order to match the experimental rate constant ratio,  $k_{a\infty}^{1H5}/k_{a\infty}^{H2}$ , of 18,  $E_0$  for 1H5 must fall between 28.1 and 28.8 kcal/mol for the "allyl" and "normal" models. For this value of  $E_0$  for the 1H5 decomposition the rate constant ratio *increases* by a factor of 1.08 for a *decrease* in  $E_0$  of 0.1 kcal/mol. This variation is approximately exponential so a decrease of 1.0 kcal/mol results in an increase in the ratio of  $(1.08)^{1.0/0.1}$  or 2.2.

#### Discussion

The reaction profile for the decomposition of H2 and 1H5 along with the appropriate energy parameters are shown in Figure 1. For comparative purposes the zero point energy levels of the radicals, H2 and 1H5, are taken to be equal. From the calculated results a difference in decomposition critical energy of H2 and 1H5 ( $\Delta E_0$ ) of 2.6  $\pm$  0.3 kcal/mol is needed to agree with the experimental rate constant ratio.  $\Delta E_0$  is also the difference in stabilization of the respective TS's. Using this value of  $\Delta E_0$  and the bond energies for a primary C-H bond and a primary allyl C-H bond as 96.2 and 87.1 kcal/mol,<sup>17</sup> respectively, the products for the 1H5 decomposition relative to the products for the H2 decomposition are stabilized  $(E_{s'})$  by 9.1 kcal/mol. Clearly the total amount of product stabilization does not appear in the TS since  $\Delta E_0 < E_{s'}$ . When considering the reverse reaction, radical + propene, the stabilized "reactants" (allyl + propene) have an  $E_0$  of 14.5 kcal/mol which is 6.5 kcal/mol greater than the normal radical + olefin  $E_0$  of 8 kcal/ mol.<sup>18</sup> The value of  $\Delta E_0$  being closer to zero than 9.1 kcal/ mol suggests that the TS is more characteristic of the associated radical than the fragments (radical and olefin). This conclusion has also been reached from normal mode calculations<sup>15</sup> in which the bond order of the breaking bond was systematically varied from 0 to 1 with resulting changes in the frequency assignments for the TS. A bond order model was found which optimized the agreement between experimental and calculated  $k_a$ 's for various experimentally observed systems;<sup>15</sup> the optimized model was found to have a bond order of 0.35 for the breaking bond.

Two studies on the decomposition of 1-penten-5-yl (1P5) have also been reported.<sup>19,20</sup> This reaction produces allyl +



Figure 2. Reaction profiles for the  $CH_3$  (Me) + 1-butene (1B) and  $CH_3$  (Me) + 1,3-butadiene (13B) systems. For comparative purposes the zero point energy levels of the 2MB1 and 3M1B4 radicals have been set equal to zero.

ethene. In the study by Watkins,<sup>19</sup> 1P5 was formed by the addition of *n*-propyl to acetylene forming 1-penten-1-yl which in turn isomerizes to 1P5. The reaction was carried out at 55° using acetylene as the deactivator; an absolute value for the decomposition rate constant was reported assuming unit collisional deactivation efficiency for acetylene and a monoenergetic input for the 1P5 radical. In the system reported by Carter and Tardy<sup>20</sup> the 1P5 was formed by the addition of H atoms to cyclopentene, forming the cyclopentyl radical which then decyclizes to give 1P5; hydrogen was the deactivator.

Both of the above 1P5 studies suffer from the fact that (i) a comparison with absolute rate constants is made, (ii) the 1P5 is not formed directly (thus producing a complex steady state population distribution), and (iii) an inefficient deactivator is present. However, when least-square calculations using the appropriate steady state populations and the appropriate weak deactivator model are performed, the critical energy for decomposition is found to be 26.3 kcal/mol. This result assumes that the calculational factor of  $2.2^3$ found for alky-2 radicals is also valid for alkyl-1 decompositions. This critical energy for decomposition gives an  $E_0$  of 14 kcal/mol for the reverse process; allyl + ethene. This value is in agreement with the results reported here for allyl + propene. A value of 14 kcal/mol results when the following factors are used in correcting Watkins' reported value of 12 kcal/mol: (i) a weak collider, (ii) a nonmonoenergetic distribution of energy states; and (iii) the "uncertain" calculational factor of 2.2 which is necessary when comparing absolute rate constants.

A system which involves stabilization in both reactant and product states is the addition of methyl to 1,3-butadiene. This system is best compared with that of methyl + 1butene. There are two reaction paths, Markovnikov (M) and anti-Markovnikov (AM) addition, producing pentyl-3 (P3) or 1-penten-3-yl (1P3) and 2-methylbutyl-1 (2MB1) or 3-methyl-1-buten-4-yl (3M1B4), respectively. The critical energies for these processes are:  $E_0^{\rm M}$  or  $E_0^{\rm MD}$  and  $E_0^{\rm AM}$  or  $E_0^{\rm AMD}$ , respectively. Figure 2 depicts these systems such that the zero point energy levels of the 2MB1 and 3M1B4 radicals are equal. The stabilization energy of 1,3butadiene (a conjugated diene),<sup>21,22</sup>  $E_{s'}$ , is between 3 and 4 kcal/mol (3.5 ± 0.5), while the stabilization energy of 1P3 (a substituted allyl radical) ( $E_s$ ) is computed to be 11.3 kcal/mol.

The Markovnikov Addition System. From thermal data  $E_0^{M}$  is 8 kcal/mol<sup>18</sup> while  $E_0^{MD15}$  is 4 kcal/mol. Thus  $\Delta E_0^{M} = E_0^{M} - E_0^{MD} + E_{s'} = 7.5 \pm 0.5$  kcal/mol. This stabilization energy suggests that the TS resembles the as-

sociated radical analogous to the 1,5-hexadiene system. Assuming that  $\Delta E_0$  has two components (energy stabilization from reactants and products) and the contributions for each are proportional to the amount of inherent stabilization of reactant and product the relative stabilization contributions can be computed. For the 1H5 system, 2.6 kcal/mol of the 9.1 kcal/mol, product stabilization energy is observed in the TS, analogously one would expect that approximately 1.0 kcal/mol from  $E_{s'}$  will be contributed to the TS stabilization in the methyl +  $C_4$  system. The remaining 6.5 kcal/ mol of TS stabilization must come from the 11.3 kcal/mol stabilization  $(E_s)$  of the 1P3 radical. Thus the absolute stabilization contributions to the TS are 28 and 58%, respectively, or in terms of *relative* contributions, the TS obtains 33 and 67% of its stabilization from the fragments (olefin + radical) and associated radical, respectively. These percentages parallel the results from normal mode calculations on bond order (0.35) of the TS for these reactions.<sup>15</sup>

Anti-Markovnikov Addition System. A previously reported<sup>23</sup> value of 34.8 kcal/mol for  $E_0^{3M1B4}$  gives a corresponding value of 11.3 kcal/mol for  $E_0^{AMD}$ . Since  $E_0^{AM} =$  $8.9 + \Delta E_0^{AM}$ ,  $E_0^{AM}$  must be between 8.9 and 12.4 kcal/ mol depending on the TS stabilization. Assuming that the stabilization for this system is similar to the stabilization in the 1H5 system, then  $\Delta E_0^{AM} = 1.1$  kcal/mol and  $E_0^{AM}$  is predicted to be 10.0 or 2.0 kcal/mol higher than the normal Markovnikov addition.

There are no experimental values which can be compared with this predicted value of  $E_0^{AM}$ ; however, it has been observed that the addition of H atoms to terminal olefins has an  $E_0^{AM}$  which is 1.8 kcal/mol<sup>24</sup> higher than that for the Markovnikov addition. Contrasted to this experimental value for H atom addition is a theoretically calculation by Flanneng.<sup>25</sup> His calculations predict that  $E_0^{AM}$  is between 1.2 and 2.5 kcal/mol lower than that for the Markovnikov addition. Work along these lines is needed to resolve the ambiguity.

#### Conclusion

Evidence is given that the TS for alkyl radicals undergoing  $\beta$  scission decompositions resembles (in terms of energy stabilization contributions) the initial radical more than the decomposition fragments. Thus if the initial radical has energy stabilization moieties which are involved in the reaction coordinate the critical energy for the process will be increased as compared with a nonstabilized specie as in the case of the carbon-carbon rupture of C=CCCC and CCCCC. The reverse reaction of radical and olefin is also affected; in this case the critical energy increases if the fragments are stabilized and there is no energy stabilization in the associated radical. On the other hand, the critical energy will decrease if the associated radical has more stabilization than the fragments. For allyl + olefin 2.6 kcal/mol of the 9.1 kcal/mol allyl stabilization energy is available to the transition state stabilization.

Using a linear relationship for stabilization contributions from reactants and products to the transition state, it was calculated that the anti-Markovnikov addition of methyl radicals to an olefin has a critical energy 2.0 kcal/mol greater than that for the Markovnikov addition.

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