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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 β 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 β 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 ± 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').



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 Rice¹ (RRKM). The first three

Table I. Summary of Experimental Results^a

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

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

Table II. Summary of Calculational Results

System (TS Model)	E_0 , kcal/mol	ΔE_0 , kcal/mol	$k_{a\infty}, \text{sec}^{-1}$		$k_{a\infty}^{1H5}/k_{a\infty}^{H2}$		$k_{a\infty}^{1H5}(\text{normal})/k_{a\infty}^{1H5}(\text{allyl})$		$\beta = k_{a\infty}(\text{SC})/k_{a\infty}(\text{400 SL})$
			400 SL	SC	400 SL	SC	400 SL	SC	
H + 1H → H2 ("normal")	31.1	0	2.45 × 10 ⁶	5.37 × 10 ⁵					0.219
H + 15H → 1H5 ("normal")	31.1	0	6.26 × 10 ⁶	1.38 × 10 ⁶	2.55	2.57	1.45	1.45	0.220
	29.1	2	3.38 × 10 ⁷	6.89 × 10 ⁶	13.80	12.83	1.45	1.45	0.204
	27.1	4	1.65 × 10 ⁸	3.12 × 10 ⁷	67.53	58.15	1.45	1.45	0.188
	25.1	6	7.5 × 10 ⁸	1.30 × 10 ⁸	306.45	242.22	1.45	1.45	0.173
H + 15H → 1H5 ("allyl")	31.1	0	4.31 × 10 ⁶	9.52 × 10 ⁵	1.76	1.77			0.221
	29.1	2	2.34 × 10 ⁷	4.76 × 10 ⁶	9.54	8.87			0.205
	27.1	4	1.14 × 10 ⁸	2.16 × 10 ⁷	46.59	40.20			0.189
	25.1	6	5.18 × 10 ⁸	9.00 × 10 ⁷	211.60	167.60			0.174

Table III. Frequency Assignments for the H2 and 1H5 Systems

Type of mode ^a	No. of modes				
	H1 system		15H system		
	H2	H2 TS	1H5	1H5 "iso-lated"	TS "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	
C=C stretch [1350] ^b		1		1	1
C—C stretch in C=C—C					1
[1300 (2)] ^b					
CH ₃ bends [1462 (2), 1374, 1168, 950]	2	2	1	1	1
H ₂ C=bends [1440, 978, 907]			1	1	1
=C—H bends [1300, 920]			1	1	1
·C—H bends [1260, 768]	1	1	1	1	1
GH ₂ bends [1450, 1310, 1260, 768]	3	1	2		
[1450, 1310, 630, 768] ^b		2		2	2
CCC bends [474, 370]	1	1	1	1	1
[303, 139]	1		1		
[152, 69] ^b		1		1	1
CC torsions [212 (2), 125, 94, 61]	1				
[212 (2), 108, 229 30] ^b		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⁻¹. ^b Designates modes which apply to TS.

where

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

is the sum of vibration-rotation energy states of the TS up to the energy in question, N_{E^+} is the density of vibration-rotation 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 calculated¹¹ from both the k_E 's and the collision transition probabilities for energy transfer. These probabilities for hydrogen have been discussed elsewhere¹¹ 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 Rabinovitch³ 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.¹⁵

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,⁷ 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 CH₃—C torsion by a CH₂=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 π 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 assignments⁷ 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-

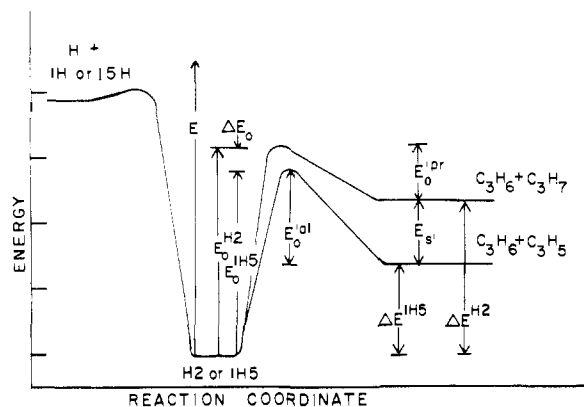


Figure 1. Reaction profiles for the H + 1-hexene (1H) and H + 1,5-hexadiene (15H) systems. For comparative purposes the zero point energy levels of the H2 and 1H5 radicals have been set equal to zero.

der (step ladder model with steps of 400 cm^{-1} ; 400 SL) are summarized in Table II. These results show that the collisional efficiency, β , as defined¹¹ 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 β decreases by $\sim 22\%$.

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 (ΔE_0) of 2.6 ± 0.3 kcal/mol is needed to agree with the experimental rate constant ratio. ΔE_0 is also the difference in stabilization of the respective TS's. Using this value of ΔE_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,¹⁷ 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.¹⁸ The value of ΔE_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 calculations¹⁵ 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;¹⁵ 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.^{19,20} This reaction produces allyl +

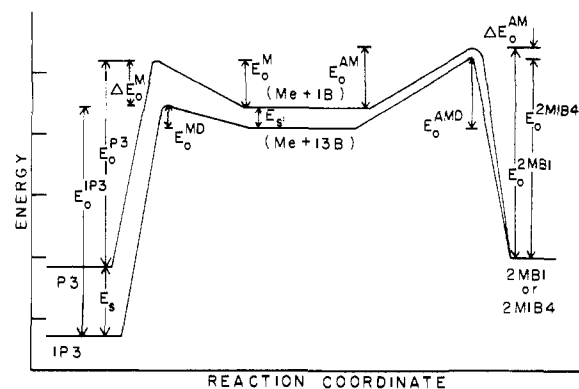


Figure 2. Reaction profiles for the CH₃ (Me) + 1-butene (1B) and CH₃ (Me) + 1,3-butadiene (13B) systems. For comparative purposes the zero point energy levels of the 2MB1 and 3M1B4 radicals have been set equal to zero.

ethene. In the study by Watkins,¹⁹ 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 Tardy²⁰ 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 2.2³ 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 + 1-butene. 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^M or E_0^{MD} and E_0^{AM} or E_0^{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 1,3-butadiene (a conjugated diene),^{21,22} 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/mol¹⁸ 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 ΔE_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.¹⁵

Anti-Markovnikov Addition System. A previously reported²³ 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/mol²⁴ higher than that for the Markovnikov addition. Contrasted to this experimental value for H atom addition is a theoretical calculation by Flanneng.²⁵ 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 β 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 $C=C\dot{C}C$ and $CCC\dot{C}C$. 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.

Acknowledgment. The author wishes to thank the Research Corporation for a grant which was used to purchase equipment used in this work. Computing funds from the University of Iowa Graduate School for the use of computing at the University Computer Center are gratefully acknowledged.

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