Localization of Excitation Energy in Chemically Activated Systems. 3-Ethyl-2-methyl-2-pentyl Radicals

M. C. Flowers[†] **and B. S. Rabinovitch***

Department of Chemistry BG-10, University of Washington, Seattle, Washington 98195
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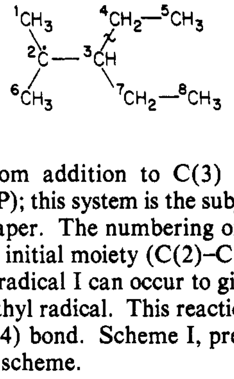
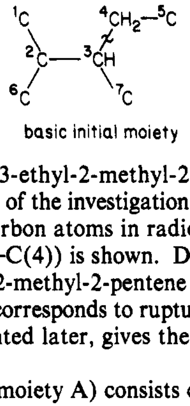
Chemically activated 3-ethyl-2-methyl-2-pentyl radicals were produced at 300 K by H-atom addition to 3-ethyl-2-methyl-2-pentene at hydrogen gas pressures of 15 to 10 800 torr. These radicals can decompose to 2-methyl-2-pentene and an ethyl radical. The initially produced radical has a nonrandom energy distribution. Our observations help to clarify the size of the initially excited subset of vibrational modes; remaining uncertainty concerns the total number of internal rotational degrees of freedom to be included. An analogy exists to single photon vibrational excitation studies.

Introduction

Recently, rates of intramolecular energy relaxation have been determined for chemically activated 3-hexyl,[1] 5-methyl-3-hexyl,[2] and 3-methyl-3-hexyl[3] radicals produced by H-atom addition to olefins. These radicals undergo competing unimolecular reactions via C–C bond ruptures. These competing reactions have different behavior on a short (picosecond) time scale, when the energy initially deposited in the radical has not yet been randomized over the whole molecule, but the same, statistical, behavior on a long time scale. A detailed rationale of the method and summary of earlier results are given in ref 1 and 4.

The intramolecular relaxation times (λ^{-1}) deduced from the competing rates depend on assumptions made regarding the choice of the initially excited vibrational subset, or moiety, of the radical. Three different three-carbon moieties were examined in previous studies (two- and four-carbon moieties were conclusively ruled out).[1-3] The basic three-carbon moiety (C(2)–C(3)–C(4)) is illustrated here for 3-ethyl-2-methyl-2-pentyl (I) radicals generated





basic initial moiety

by H-atom addition to C(3) of 3-ethyl-2-methyl-2-pentene (3E2M2P); this system is the subject of the investigation reported in this paper. The numbering of carbon atoms in radical I and the basic initial moiety (C(2)–C(3)–C(4)) is shown. Decomposition of radical I can occur to give 2-methyl-2-pentene (2M2P) and an ethyl radical. This reaction corresponds to rupture of the C(3)–C(4) bond. Scheme I, presented later, gives the detailed reaction scheme.

The smallest moiety considered (moiety A) consists of all the vibrations of an isolated species having the structure of the basic initial moiety, including internal rotations about C(2)–C(3) and C(3)–C(4), but excluding the three skeletal bends about C(2), i.e., the total number of vibrations = $3N - 9 = 21$. The vibrational frequencies of the moiety constituted a subset of the vibrational frequencies of radical I.

Moiety B is the same as moiety A but includes the three skeletal bends excluded in A.

Moiety C is the largest moiety that can be expected to be formed[2] and is the same as B but includes also additional torsions about C(1)–C(2), C(6)–C(2), and C(4)–C(5), and an ethyl torsion about C(3)–C(7).

Moieties in the earlier radical systems studied in this laboratory differ from the above only in as much as different substitutents were present at C(2), C(3), and C(4). Conflicting conclusions were reached in these studies. In the case of 5-methyl-3-hexyl radicals,[2] produced from H-atom addition to *cis*-5-methyl-2-hexene and *trans*-2-methyl-3-hexene, moieties A and B were preferred ($\lambda^{-1} \simeq 0.08$ and 0.14 ps, respectively) over moiety C ($\lambda^{-1} = 0.25$ ps for *cis*-5-methyl-2-hexene precursor and 0.59 ps for *trans*-2-methyl-3-hexene precursor), mainly because of the agreement between the relaxation times obtained in the two former cases for the different (isomeric) precursor molecules. The relaxation time for moiety A, however, seems somewhat small and B is probably preferred. In the case of the study of 3-methyl-3-hexyl radicals,[3] moiety B gave a similar, somewhat small values, $\lambda^{-1} = 0.07$ ps (an even smaller, and probably physically unrealistic, value for moiety A was deduced), but a value of 0.13 ps for moiety C. Moiety C was thus preferred in this instance.

There is an analogy here between the indecision associated with the size of the initially excited moiety in chemical activation and the uncertainty regarding the extent and nature of the initial mixing and coupling of the primary accepting mode(s) with other mode(s) in single-photon, multiquantum, excitation experiments; thus, for example, "C–H overtone" excitation in benzene[5a] produces a mixed state that is neither a C–H molecular eigenstate nor a "good" local mode.

In an attempt to clarify further the size of the initial subset of excited vibrations in a chemical activated system, we have studied the decomposition of a more highly branched radical than heretofore investigated, where discrimination between the various moieties is hopefully enhanced by increased substitution within the moiety. Concomitantly, the pressure region of greatest interest, where effects due to nonrandomization of energy might be observed, is shifted to more difficulty accessible higher pressures. To anticipate, our fondest hopes have not been realized but, nonetheless, our results and conclusions appear worthy of dissemination.

Experimental Section

3-Ethyl-2-methyl-2-pentene (3E2M2P) and 2,3-dimethyl-2-butene (23DM2B) (Wiley Organic) were purified by GLPC on a 1 ft × $^1/_2$ in. column of 20% squalane on Chromosorb P at 70 and 50 °C, respectively. Hydrogen (Arco) was purified by passage over a hot "active" copper and through molecular sieve at 77 K.

The reaction vessel was a 2-mm wall, 20-mL volume, silica tube containing 0.05 mL of mercury. A stock reaction mixture con-

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[†] Permanent address: Department of Chemistry, The University, Southampton S09-5NH, U.K.

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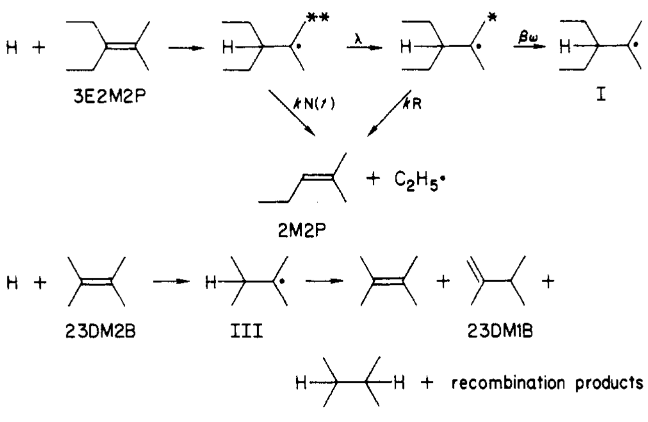
Scheme I



sisting of 0.0024% 23DM2B and 1% 3E2M2P in hydrogen was stored in a darkened 2-L flask and used for all runs. Reaction mixtures were made up by taking 15–60 torr of the stock mixture and adding hydrogen to it to give the required total pressure. Hydrogen atoms were produced by Hg($^3P_1$) photosensitized reaction by irradiation of the reaction mixture with a 8-W low-pressure mercury lamp.

Reactions products were analyzed by gas chromatography on a 150-ft squalane SCOT column preceded by an additional 50-ft squalane precolumn, with use of photoionization detection; both columns were maintained at 30 °C. The precolumn was used to trap 3E2M2P and long retention time products, and was backflushed at a predetermined time after the start of the analysis. When backflushing, a ballast column was inserted in series with the main column in order to maintain constant flow rates. Great care was necessary to eliminate from the system impurity peaks with retention times similar to those of the decomposition product, 2-methyl-2-pentene (2M2P). In preliminary work such peaks were found to arise from the photosensitized reaction of unknown impurities in the hydrogen. It was for this reason that molecular sieve at 77 K was used in the hydrogen purification chain.

Reaction Scheme and Experimental Rationale

Scheme I summarizes the reaction scheme. Radicals having nonrandomized energy are indicated by two asterisk superscripts whereas energized radicals with randomized energies have a single asterisk. β represents the collision efficiency of the bath gas and ω the collision frequency, where the rate of reaction of the nonrandomized initial species, $k_N(t)$, is specifically considered time dependent as energy relaxation proceeds.[4]

H-atom addition to 3E2M2P gives rise to 3-ethyl-2-methyl-2-pentyl (I) and 3-ethyl-2-methyl-3-pentyl (II) (not shown) radicals. II can decompose by two channels, only one of which has a component rate from the initially nonrandomized species. It is thus a system entirely analogous to those previously investigated.[1-3] Unfortunately the combination of analytical difficulties involving impurity and product peaks occurring at the same, or at very similar, retention times to the desired product, and the fact that the yield of products from these reactions was low, resulted in the study of the reactions of II not being practicable. We therefore investigated the reaction of I.

Compound I can decompose by loss of an ethyl radical to give 2M2P with both random (rate constant k_R) and nonrandom (rate constant $k_N(t)$) energy distribution components. However, as there is no internal reference reaction available (i.e., a reaction that can only occur when energy has randomized over the entire molecule), 23DM2B was added to the system to provide a standard reference reaction. 23DM2B was chosen as it would be expected to have a very similar (equal) rate of H-atom addition as the main reactant. 2,3-Dimethyl-1-butene (23DM1B), a disproportionation product of 2,3-dimethyl-2-butyl radicals (III), was used to monitor the amounts of reaction. 2,3-Dimethylbutane could not be used for this purpose as there was a considerable contribution to this peak from a product of reaction of 3E2M2P. Based on previous estimates of the ratio 23DM1B to 23DM2B (5.5) and the disproportionation/recombination ratio (3.0) for III,[6] and on the assumption that the rates of disproportionation are proportional to the number of abstractable H-atoms, we estimate the total amount of reaction of 23DM2B is given by the yield of 23DM1B multiplied by 2.6. Previous work[6] has established that under all conditions of the present study chemically activated decomposition of III will not be a significant source of loss of these species.

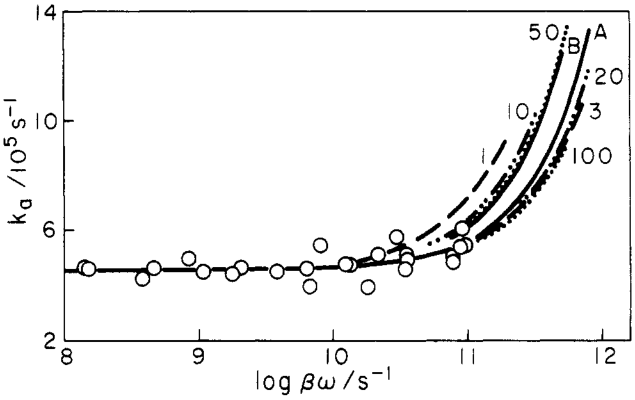


Figure 1. Experimental and calculated dependence of k_a on effective collision frequency ($\beta\omega$). Solid line A, least-squares fit of experimental data to a linear k_a vs. $\beta\omega$ plot; solid line B, least-squares fit of experimental data to a linear k_a vs. $\beta\omega$ plot but with slope arbitrarily increased 2σ from best fit; ···–, calculated curves for moiety A; –··–··, calculated curves for moiety B; – – –, calculated curves for moiety C. Numerical values cited on the graph are evalues of $\lambda/10^{12}$ s^{-1}. Curves closer to lines A and B were calculated for each moiety but are not reproduced here for reasons of clarity. The values of λ displayed were chosen so as to encompass curves A and B and to mutually interfere as little as practical.

Using Scheme I, and assuming a steady state in all radical concentrations, we may deduce the following expression:

$$k_a = \frac{2\beta\omega[\mathrm{2M2P}][\mathrm{23DM2B}]}{2.6[\mathrm{23DM1B}][\mathrm{3E2M2P}]} = k_R(1 + k_N/\lambda) + k_N\beta\omega/\lambda \qquad (1)$$

where k_a represents the measured decomposition rate constants, k_N is a time-averaed representation of $k_N(t)$; square brackets signify concentrations of species; and the factor 2 allows for H-atom addition path degeneracy. Hence a plot of k_a vs. ω should be linear. As the data obtained extend over a wide pressure range, plots of k_a vs. log ω have normally been used to display the data, with "turn up" in these plots indicating the onset of significant rate contributions from the nonrandomized species.

Results

The yields of 2M2P and 23DM1B were measured at total pressures between 15 and 10 800 torr. The extent of reaction ranged between 2% and 15%. In these and in other preliminary runs we could detect no change in the data as a function of percentage reaction. The values of k_a are plotted vs. log (pressure/torr) in Figure 1. The collision efficiency of hydrogen was assumed to be[1-3] 0.2 and the collision diameters of hydrogen and 3E2M2P radicals were taken equal to 2.92 and 6.58 Å, respectively.

The uncertainty in the values of k_a at lower pressure is probably <10%, but at pressures above 700 torr it is in the range 10–25%. Within the uncertainty of the data, k_a shows no pressure dependence in the range investigated, as would not be unexpected for such large moieties as arise here. However, if the data are fitted to eq 1, with k_R = 4.5 × 10^5 s^{-1}, the solid curve A in Figure 1, then represents the best fit. Curve B shows the pressure dependence if the slope of the linear plot is shifted by two standard deviations from the best fit.

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TABLE I: Frequency Assignments for 3-Ethyl-2-methyl-2-pentyl Radical, H-Atom Association Complex and Decomposition Complexes (cm^{-1})

3E2M2P radical	H-assoc complex[a]	decomp complex[a]
2964 (8)		
2928 (2)		
2904	rc	
2882 (4)		
2854 (2)		
1462 (8)		
1450 (2)		
1374 (4)		
1346 (2)	150 (2)	
1310 (2)		
1260 (2)		1260, 630
1168 (4)		
1050 (2)	1050	
950 (6)	950 (8)	
850 (2)	850	rc, 850
768 (2)		
750	1320	1200
477 (2)		477, 238
461	505	
365	310	
351	385	175
260	302	
212 (2)		
200 (2)		
188 (2)	160, 218	188, 94
130 (2)		130, 65
78		189

[a] Only changes from the radical are shown.

Calculations

The basic methodology has been given in detail before.[1-4] The frequency assignments, required for the calculation of rate constants, for the radical, H + olefin in association complex and decomposition complex are listed in Table I, and those for moieties A, B, and C, and the corresponding association and decomposition complexes are given in Table II. [Moieties B and C correspond to moieties 2 and 3 in ref 1 and 2, and to A and B in ref 3. Moiety A corresponds to moiety 1 in ref 1 and 2.]

The critical energy (E_0) was estimated to be 26.8 kcal mol^{-1} by use of the following values deduced from previous, related considerations.[7-10]

$$\Delta H_f{}^{\circ}{}_0(C_2H_6) = -16.5 \text{ kcal mol}^{-1}$$

$$\Delta H_f{}^{\circ}{}_0(\text{2M2P}) = -8.0 \text{ kcal mol}^{-1}$$

$$\Delta H_f{}^{\circ}{}_0(\text{3-ethyl-2-methylpentane}) = -38.0 \text{ kcal mol}^{-1}$$

$$D^{\circ}{}_0(C_2H_5\text{–H}) = 97.0 \text{ kcal mol}^{-1}$$

$$D^{\circ}{}_0(\text{3-ethyl-2-methyl-2-pentyl-H}) = -91.6 \text{ kcal mol}^{-1}$$

$$E_0(\text{addition of ethyl radicals to 2M2P}) = 8 \text{ kcal mol}^{-1}$$

The minimum excess energy ($E_{\min}$) of the chemically activated radical was then chosen so that, with a path degeneracy of 2, good agreement was obtained with the experimental and calculated k_R. With $E_{\min}$ = 34.5 kcal mol^{-1}, k_R(calcd) = 4.6×10^5 s^{-1}. Then for moiety A, $k_N(0) = 8.3 \times 10^8$ s^{-1}; while for moiety B, $k_N(0) = 1.7 \times 10^8$ s^{-1}, and for moiety C, $k_N(0) = 2.2 \times 10^7$ s^{-1}.

Some representative calculated k_a vs. log pressure curves are shown in Figure 1. We estimate, using these curves, that for moiety B, $\lambda > 1.1 \times 10^{13}$ s^{-1} (curve B), with a best fit to the data of 1.7×10^{13} s^{-1} (curve A); for moiety C, $\lambda > 1.6 \times 10^{12}$ s^{-1} (curve B), with a best fit to the data of 2.4×10^{12} s^{-1} (curve A); and for moiety A, $\lambda > 5 \times 10^{13}$ s^{-1} (curve B), with a best fit to the data of 8×10^{13} s^{-1} (curve A). Any uncertainties in the thermochemistry and absolute values of k_R will affect these conclusions very little. If, for example, E_0 is lowered by 1 kcal mol^{-1}, with all other parameters left unchanged, the k_R(calcd) is raised by a factor of 2.5 to 1.16×10^6 s^{-1}, but the values of λ then needed to fit the data are shifted to lower values by only 15% and 10% for moieties B and C, respectively.

TABLE II: Frequency Assignments for the Nascent Moiety B, H-Association Complex, and Decomposition Complexes (cm^{-1})

moiety B[a]	H-assoc complex[b]	decomp complex[b]
2928		
2854		
2904	rc	
1450		
1346 (2)	150 (2)	
1310		
1260		630
1050 (2)	1050	
950	950 (3)	
850 (2)	850	rc, 850
768		
750	1320	1200
477		238
461	505	
365	310	
351	385	175
260	302	
188 (2)	160, 218	188, 94
130		65
78	240	189

[a] Moiety C has additional torsions at 212, 200 (2), and 130 and moiety A has bends at 461, 365, and 260 deleted. [b] Only changes from moiety B are shown.

Discussion

Although the data obtained here do not yield absolute values for the intramolecular relaxation rates, the results do assist in clarifying the conclusions reached in the previous studies. Namely, it is clear that the relaxation rates for the smallest moiety (A) are higher than could be considered physically reasonable. Moreover, the relaxation time calculated here (12.5 fs) is four times lower than that reported[11] for "ultrafast" vibrational relaxation in tetramethyldioxetane (a molecule of similar complexity and structure to the present subject), excited by overtone absorption in the CH stretch region to a comparable level of vibrational excitation. Since any difference between the two phenomena should work in the opposite direction, this moiety is not considered a suitable representation of the initially excited vibrational subset; it is too small. Moiety B gives a value of λ that is somewhat high but, as has been previously suggested,[3] high values of λ may well be the consequence of a high degree of branching in the radical at the site of activation. Moiety C, the favored moiety in the previous study,[3] with a value of $\lambda > 2 \times 10^{12}$ s^{-1} is still also a plausible representation of the initial moiety as a consequence of this work. It is to be regretted that we were unable to extend the study to higher pressures that could have provided more definitive discrimination between B and C; the analytical difficulties simply became overwhelming. In summary, the residual uncertainty concerns the number of additional internal rotations to be included in the specification of the initially excited vibrational subset.

Acknowledgment. This work was supported by the National Science Foundation.

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