Experimental and Theoretical Study of the sec-C₄H₉ \rightleftharpoons CH₃ + C₃H₆ Reaction

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The kinetics of the unimolecular decomposition of the $sec-C_4H_9$ radical has been studied experimentally in a heated tubular flow reactor coupled to a photoionization mass spectrometer. Rate constants for the decomposition were determined in time-resolved experiments as a function of temperature (598-680 K) and bath gas density $((3-18) \times 10^{16} \text{ molecules cm}^{-3})$ in three bath gases: He, Ar, and N₂. The rate constants are in the falloff region under the conditions of the experiments. The results of earlier studies of the reverse reaction were reanalyzed and used to create a transition state model of the reaction. This transition state model was used to obtain values of the microcanonical rate constants, k(E). Falloff behavior was reproduced using master equation modeling with the energy barrier height for decomposition (necessary to calculate k(E)) obtained from optimization of the agreement between experimental and calculated rate constants. The resulting model of the reaction provides the high-pressure limit rate constants for the decomposition reaction $(k^{\infty}_{1}(sec-C_{4}H_{9} \rightarrow C_{3}H_{6} + CH_{3}) = 2.73 \times 10^{10}T^{1.11} \exp(-15712 \text{ K/T}) \text{ s}^{-1})$ and the reverse reaction $(k^{\infty}_{-1}(CH_{3}$ + $C_3H_6 \rightarrow sec-C_4H_9$ = 2.13 × 10⁻¹⁹ $T^{2.28} \exp(-3319 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Average values of $\langle \Delta E \rangle_{down}$ = 363 (He), 447 (Ar), and 506 cm⁻¹ (N₂) for the average energy loss per deactivating collision were obtained using an exponential-down model. Parametrization of the temperature and pressure dependence of the unimolecular rate constant for the temperature range 298-1500 K and pressures 0.001-10 atm in He, Ar, and N₂ is provided using the modified Lindemann-Hinshelwood expression.

I. Introduction

In high-temperature combustion processes, the unimolecular decomposition of polyatomic free radicals competes with other elementary reactions involving these same intermediates (e.g., their reactions with O_2 , atoms, and other free radicals).¹⁻³ In any quantitative combustion modeling study, the proper inclusion of the kinetics of these reactions, including the pressure and temperature depencies of their unimolecular rate constants, is essential.^{4,5} The ultimate products formed by combustion processes, rates of burning, and temperature dependencies of flame properties are sensitive functions of the relative importances of these competing processes.

Most of our current knowledge of the behavior of these unimolecular reactions (e.g., rate constants, falloff characteristics) is derived from kinetic data on the reverse addition reactions combined with thermodynamic properties of the reactants and products.⁶ In general, the kinetic data on the reverse reactions have been obtained at much lower temperatures than those of combustion processes and under conditions which are at or near the high-pressure limit. Major temperature and density extrapolations of the rate constants and the falloff characteristics of the unimolecular rate constant so derived are required to obtain rate constants that can be used for modeling hightemperature chemical processes.

We have developed an experimental procedure to isolate and quantitatively study the kinetics of the unimolecular decomposition of free radicals at elevated temperatures (up to ≈ 1100 K in selected cases) and at low pressures (1-10 Torr) where falloff from the high-pressure limit can be significant.^{7,8} Rate constants are measured as a function of temperature and bath-gas density. Falloff behavior is analyzed using a master equation approach to characterize weak-collision effects. It has been possible in favorable cases to obtain not only a temperature-averaged value of $\langle \Delta E \rangle_{\rm down}$, the average internal energy lost in deactivation collisions, for the conditions of the experiments but also an indication of the temperature dependence of this parameter.^{9,10} Such temperature dependencies are needed to extrapolate weak-collision effects observed under the relatively mild experimental conditions used in laboratory studies to the harsher conditions of combustion processes. To date, we have studied the unimolecular decomposition of the following radicals: HCO,⁷ *n*-C₅H₁₁,⁸ C₂H₅,⁹ *i*-C₃H₇,¹⁰ *n*-C₃H₇,¹¹ CH₃CO,¹² CH₃CHCl,¹³ and *t*-C₄H₉.¹⁴

We report here on the results of our current investigation, that of the unimolecular decomposition of the *sec*-C₄H₉ radical:

$$sec-C_4H_9 \rightleftharpoons CH_3 + C_3H_6$$
 (1, -1)

Rate constants for reaction 1 were measured at four densities of He ([He] = $(3-18) \times 10^{16}$ molecules cm⁻³) and at three densities of N₂ and Ar ([N₂], [Ar] = $(3-12) \times 10^{16}$ molecules cm⁻³) in the temperature range 598–680 K. Data analysis involved creation of a transition state model which reproduces the temperature dependence of the high-pressure-limit rate constants of the reverse reaction -1. The thermochemistry of reaction 1,-1 was reanalyzed based on the data available in the literature as well as on modeling of our experimental results on reaction 1. A transition state model was used to provide k(E) values which were then used in the master equation analysis of the weak-collision effects in the observed falloff behavior of the experimentally measured rate constants.

The unimolecular decomposition of the *sec*-C₄H₉ radical has not been isolated for direct study prior to this investigation. However, the rate constant for *sec*-C₄H₉ dissociation relative to that for recombination has been determined by both Gruver and Calvert^{15,16} and Lin and Laidler¹⁷ while Gierczak et al.¹⁸ reported the rates of unimolecular decomposition and isomerization. Each of these investigations involved the study of complex reaction systems and will be discussed in detail in section III.

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The reverse reaction -1, addition of CH₃ radicals to the double bond of propene, has been studied by several groups. Miyoshi and Brinton¹⁹ and Cvetanovic and Irwin²⁰ determined overall (not site-specific) rate constants for the addition reaction. Terminal addition of methyl radicals to propene has been investigated by Tedder et al.²¹ whereas Baldwin et al.²² report both terminal and nonterminal addition rate constants. Each of these studies measured the addition rate constants relative to a different reference reaction as will be discussed in detail in section III.

Recommendations for the temperature dependence of the rate constant of reaction 1 have been provided by Warnatz¹ (based on the results of Lin and Laidler¹⁷) and by Tsang⁶ (based on analysis of the kinetics of the reverse reaction and the entropy of reaction (1,-1).

We have reanalyzed these relative studies of both the direct and reverse reaction 1,-1 using new data available on the kinetics of the corresponding reference reactions. This analysis together with the modeling of our experimental data resulted in recommendations for the high-pressure-limit rate constants of reaction 1,-1 as well as in information on weak-collision effects.

II. Experimental Study

Details of the experimental apparatus²³ and procedures⁸ used have been described before and so are only briefly reviewed here. The *sec*-butyl radicals were produced homogeneously at elevated temperatures in a heatable quartz tubular reactor by pulsed laser photolysis, and their unimolecular decay was subsequently monitored in time-resolved experiments using photoionization mass spectrometry.

Pulsed unfocused 193 or 248 nm radiation (≈ 5 Hz) from a Lambda Physic EMG 201MSC excimer laser was directed along the axis of a heatable quartz reactor (1.05 cm i.d.) coated with poly(dimethylsiloxane) (PDMS) or boric acid. Gas flowing through the tube at ≈ 4 m s⁻¹ contained the radical precursor (<0.2%) and the inert carrier gas (He, Ar, or N₂) in large excess (>99.8%). The flowing gas was completely replaced between laser pulses.

The sec-butyl radicals were produced by the pulsed, 193 nm laser photolysis of 3-methyl-2-pentanone

$$C_2H_5CH(CH_3)COCH_3 \xrightarrow{193 \text{ nm}} sec-C_4H_9 + \text{ other products}$$
 (2)

or 248 nm laser photolysis of 2-bromobutane.

$$C_2H_5CHBrCH_3 \xrightarrow{248 \text{ nm}} sec-C_4H_9 + \text{ other products}$$
 (3)

The nature of the radical precursor had no influence on the observed kinetics of the *sec*-butyl radicals. Initial conditions (precursor concentration and laser intensity) were selected to provide low radical concentrations ($\leq 10^{11}$ molecules cm⁻³). Under these conditions reactions between radical products (including *sec*-C₄H₉ + *sec*-C₄H₉) had negligible rates compared to that of the unimolecular decomposition of the *sec*-C₄H₉ radicals.

Gas was sampled continuously through a conical hole (0.043 cm diameter at the inside of the reactor) in the side of the reactor and formed into a beam by a skimmer before the gas entered the vacuum chamber containing the photoionization mass spectrometer. As the gas beam traversed the ion source, a portion was photoionized and mass selected. *sec*-Butyl radicals were ionized using the light from a bromine resonance lamp (7.6–7.9 eV) with a sapphire window. Temporal ion signal

profiles were recorded on a multichannel scaler from a short time before each laser pulse up to 20 ms following the pulse. Data from 2000 to 36 000 repetitions of the experiment were accumulated before the data were analyzed.

The gases used were obtained from Aldrich (3-methyl-2pentanone, 99%; 2-bromobutane, 99%) and Matheson (He, >99.995%; Ar, >99.998%; N₂, >99.998%). Precursors were purified by vacuum distillation prior to use. Helium, argon, and nitrogen were used as provided.

The *sec*-butyl ion signal profiles were fit to an exponential function $([sec-C_4H_9]_t = [sec-C_4H_9]_0e^{-k'})$ using a nonlinear least-squares procedure. Experiments were performed to establish that the decay constants did not depend on the nature or concentration of precursor (provided that the concentration was kept low enough to ensure that radical-radical reactions had negligible rates), laser wavelength, or the laser intensity. The exponential decay constants depended only on temperature and bath gas density.

Unimolecular decay of sec-C₄H₉ was observed only above 560 K. Below this temperature a slow decay of sec-C₄H₉ is observed due to a first-order heterogeneous wall-loss process:

$$sec-C_4H_9 \rightarrow heterogeneous loss$$
 (4)

Above 560 K the decay constant increased rapidly with rising temperature due to the increasing importance of the thermal decomposition of the *sec*-butyl radical (reaction 1). The *sec*- C_4H_9 decay constants were analyzed assuming that the *sec*-butyl radicals were consumed only by two elementary reactions, (1) and (4). At low temperatures, only the heterogeneous loss is observed ($k' = k_4$). Above 560 K the sum of the two loss processes is observed ($k' = k_1 + k_4$).

Calculations of k_1 from measurements of k' require knowledge of k_4 above 560 K. While k_4 was directly determined below 560 K (10-55 s⁻¹, independent of temperature), it could not be measured above this temperature due to the additional loss of radicals by unimolecular decomposition. Values of k_4 above 560 K needed to determine k_1 from the measurements of k' were obtained by an extrapolation assuming that k_4 retains its temperature independence beyond 560 K up to the highest temperature of this study, 680 K. To minimize possible errors in the determination of k_1 caused by this assumed temperature independence of k_4 above 560 K, experiments to obtain k_1 were conducted at temperatures sufficiently high to assure that $k' \ge$ $3k_4$. It was this criterion that established the lowest temperature used to determine k_1 at each bath gas density. The highest temperature used at each total gas density was determined by the fact that decay constants above 500 s^{-1} could not be measured accurately.

A potentially complicating factor in these experiments is the production of other butyl radical isomers during the photolysis process. The most intense lines in the spectrum of a bromine ionization lamp with a sapphire window (used in the current study) lie in the region 7.59-7.87 eV,²⁴ although there are several weak components at higher energies. The only two isomers of butyl radical that have ionization potentials (IPs) low enough to be detected with a sensitivity sufficient for kinetic measurements using a bromine lamp are $t-C_4H_9$ (IP = 6.70 eV) and sec-C₄H₉ (IP = 7.25 eV).²⁵ We studied the relative sensitivity of our experimental ion detection system for the four isomers of butyl radical using bromine and chlorine ionization lamps. The methods of generating the tert-butyl radicals were described earlier.¹⁴ The $n-C_4H_9$ and $i-C_4H_9$ radicals were generated using the 248 nm photolysis of the corresponding bromides. The detection sensitivities obtained with the bromine and chlorine ionization lamps differed only by a factor of 2 for

TABLE 1: Conditions and Results of Experiments To Measure the Unimolecular Rate Constants (k_1) of the Thermal Decomposition of *sec*-Butyl Radicals in Three Bath Gases

					master						master
					analysis						analysis
10 ⁻¹⁶ [M]		10 ⁻¹³ [precursor]	k₄	k_1	$\langle \Delta E \rangle_{\rm down}$	10^{-16} [M]		10 ⁻¹³ [precursor]	k₄	k_1	$\langle \Delta E \rangle_{\rm down}$
(molecules cm ⁻³)	T (K)	(molecules cm ⁻³)	(s^{-1})	(s^{-1})	(cm^{-1})	(molecules cm ⁻³)	$T(\mathbf{K})$	(molecules cm ⁻³)	(s ⁻¹)	(s^{-1})	(cm^{-1})
					He as B	lath Gas					
3	620	3 24	18.4	65.5	379	12	630	4.0	51.8	147.0	304
3	630	3.24	18.4	106.3	448	12	630	3.9	33.0	168.6	384
3	640	3.24	18.4	124.3	359	12	630	0.46 ^a	16.3	189.3	457
3	650	3.24	18.4	171.7	364	12	640	3.0	18.0	228.4	356
3	660	3.24	18.4	253.0	404	12	640	1.7	20.1	228.0	354
3	670	3.24	18.4	327.3	390	12	640	4.0	33.9	218.3	332
3	680	3.24	18.4	389.1	348	12	640	0.46^{a}	16.3	232.0	365
6	610	3.1	18.0	58.3	337	12	650	3.0	18.0	316.6	355
6	620	3.1	18.0	85.3	346	12	650	1.7	20.1	292.5	317
6	620	3.9	27.0	94.8	403	12	650	4.0	32.9	305.6	337
6	630	3.1	18.0	126.3	380	12	650	0.46 ^a	16.3	309.6	343
6	630	3.9	24.6	133.1	401	12	660	3.0	18.0	416.0	342
6	640	3.1	18.0	171.7	359	12	660	1.7	20.1	401.5	321
6	640	3.9	24.6	192.7	421	18	600	3.3	16.4	65.5	409
6	650	3.1	18.0	244.7	376	18	600	3.3	13.3	66.3	417
6	650	3.9	22.0	250.1	388	18	610	3.3	13.3	97.6	408
6	660	3.1	18.0	295.6	324	18	610	3.3	16.4	89.7	351
6	670	3.1	18.0	410.6	339	18	620	3.3	16.4	127.7	337
12	600	3.0	18.0	50.1	318	18	620	3.3	16.4	127.0	334
12	600	1.0	19.2	52.2	348	18	620	3.3	13.3	135.7	3/0
12	610	3.0	18.0	19.1	304	18	630	3.3	10.4	192.5	202
12	610	1.0	19.2	/3.0	319	10	630	3.3	13.5	193.3	255
12	620	0.4-	12.7	108 2	401	10	640	3.3	15.5	200.8	333
12	620	5.0	10.0	100.2	327	18	650	3.3	16.4	364.7	347
12	620	1.0	33.0	109.0	304	18	650	33	133	385 9	376
12	630	3.0	18.0	161.2	349	18	660	33	16.4	456.8	300
12	630	1.7	20.1	148.3	308	10	000	5.0	10/1	12010	200
						ath Cos					
2	620	5 1	21.6	61.6	Ar as D	aun Gas	650	4.0	24.8	247 4	405
3	620	5.1	21.0	78 /	307	12	600	4.9	24.0	45 5	350
3	640	5.1	21.0	132.0	512	12	610	57	27.1 24.1	70.3	304
3	650	5.4	26.3	174.6	489	12	620	57	24.1	106.2	412
6	610	49	20.5	55.4	408	12	630	5.4	21.6	159.7	451
6	620	4.9	24.8	88.0	475	12	640	5.4	21.6	236.1	487
ő	630	4.9	24.8	114.8	422	12	650	5.4	21.6	320.9	471
6	640	4.9	24.8	175.6	481			••••			
					N. oc P	lath Gas					
3	618	13	24.4	67.2	526	6	618	37	22.4	00.3	516
3	620	4.3	24.4 74.4	70.3	493	6	628	3.7	20.0	132.0	536
3	628	43	24.4	90.7	478	6	638	3.2	20.0	182.0	518
3	630	43	24.4	100.4	503	6	648	3.7	22.4	239.0	477
3	638	43	24.4	132.6	513	ő	650	3.8	23.8	237.9	433
3	640	4.3	24.4	135.4	482	6	658	3.7	22.4	318.3	460
3	648	4.3	24.4	172.9	478	12	598	5.1	23.2	55.7	548
3	658	4.3	24.4	224.7	454	12	608	5.1	23.2	77.6	481
3	668	4.3	24.4	314.1	479	12	618	5.1	23.2	114.2	505
6	598	3.2	20.0	44.9	564	12	628	5.1	23.2	174.0	549
6	608	3.2	20.0	63.3	543	12	638	5.1	23.2	226.4	470
6	618	3.2	20.0	105.2	679	12	648	5.1	23.2	307.8	452

^a 3-Methyl-2-pentanone was used as radical precursor. 2-Bromobutane was used in all other experiments.

both $t-C_4H_9$ and $sec-C_4H_9$ isomers (with better sensitivity obtained using the chlorine lamp). Although both $n-C_4H_9$ and $i-C_4H_9$ radicals could also be detected using the bromine lamp, the sensitivity in this case was approximately 20 times lower than that obtained if the more energetic (8.6-8.9 eV) chlorine lamp was used.

Under our experimental conditions the four isomers of the butyl radical thermally decompose to a measurable extent at different temperatures. We studied the unimolecular decomposition of t-C₄H₉ earlier using the same experimental technique at T = 712-779 K.¹⁴ The decomposition of the *n*-C₄H₉ radical was studied²⁶ at T = 560-620 K, and the *i*-C₄H₉ isomer decomposes within approximately the same temperature range.

The current study of the thermal decomposition of the *sec*-C₄H₉ radical was limited to the 600–680 K temperature range. Use of the bromine ionization lamp, together with the different temperature ranges in which the four butyl radical isomers decompose, permits us to eliminate the potential contribution of other butyl radical isomers to the *sec*-C₄H₉ signal under the conditions of our experimental study.

Propene (C₃H₆) was detected as a primary product of the unimolecular decomposition of the *sec*-C₄H₉ radical with the rise time of C₃H₆⁺ matching that of the decay of the *sec*-butyl ion signal. No formation of C₂H₅ (which is a primary product of the unimolecular decomposition of the *n*-C₄H₉ isomer²⁶) was observed in the current study.



Figure 1. Plot of *sec*-C₄H₉ unimolecular rate constants (k_1 vs 1000/*T*) for different He densities (atoms cm⁻³). Lines represent the results of master equation simulation using the temperature dependence of $\langle \Delta E \rangle_{down}$ given by formula VIa. Open circles, [He] = 3 × 10¹⁶ molecules cm⁻³; closed circles, [He] = 6 × 10¹⁶ molecules cm⁻³; open triangles, [He] = 12 × 10¹⁶ molecules cm⁻³; closed triangles, [He] = 18 × 10¹⁶ molecules cm⁻³.



Figure 2. Plot of *sec*-C₄H₉ unimolecular rate constants (k_1 vs 1000/*T*) for different densities of Ar and N₂ (molecules cm⁻³). Lines represent the results of master equation simulation using the temperature dependence of $\langle \Delta E \rangle_{down}$ given by formulas VIb and VIc. Open circles, [M] = 3 × 10¹⁶ molecules cm⁻³; closed circles, [M] = 6 × 10¹⁶ molecules cm⁻³; open triangles, [M] = 12 × 10¹⁶ molecules cm⁻³.

The results of all the experiments and conditions used to determine k_1 are given in Table 1. The unimolecular rate constants for reaction 1 obtained from these sets of experiments conducted at different densities are shown in Figures 1-4. Estimated uncertainties in the k_1 determinations vary from $\pm 10\%$ in the middle of the temperature range to $\pm 20\%$ at the extreme temperatures used.

III. Data Analysis

Weak-collision effects in reaction 1,-1 (falloff from the highpressure limit) were analyzed using master equation modeling. In this section knowledge of the high-pressure limit rate constants $(k^{\infty}_1, k^{\infty}_{-1})$ is first reviewed. Then, a transition state model is created which reproduces the high-pressure-limit rate constants of the reverse (association) reaction $k^{\infty}_{-1}(T)$. The density-of-states and sum-of-states functions of the *sec*-butyl



Figure 3. Falloff curves, k_1 vs [He], for nine temperatures used in the experiments (600-680 K). Lines represent the results of master equation simulation using the temperature dependence of $\langle \Delta E \rangle_{down}$ given by formula VIa.



Figure 4. Falloff curves, k_1 vs [M] (M = Ar, N₂), for temperatures used in the experiments (600-650 K with Ar as bath gas; 598-668 K with N₂ as bath gas). Lines represent the results of master equation simulation using the temperature dependence of $\langle \Delta E \rangle_{down}$ given by formulas VIb and VIc.

radical and the transition state, needed for the calculation of k(E) values and further analysis, are obtained from the rovibrational models of these species. The hindered internal rotors are treated classically using the simple formalism introduced by us earlier.¹⁴ The transition state model provides the values of the microcanonical rate constants, k(E), needed in the master equation modeling. The energy barrier height for the decomposition reaction is obtained by an optimization. In this optimization procedure, the experimental rate constants are reproduced by master equation/RRKM modeling, and the deviation between the experimental and calculated values is minimized. Finally, the selected model of reaction 1,-1 is used to obtain quantitative information on the weak-collision effects.

1. Experimental High-Pressure-Limit Rate Constant of Reaction 1,-1. Present knowledge of the kinetics of reaction 1,-1 is based on relative rate studies. In this section we review the relevant literature and reanalyze the relative rate measurements in light of current kinetic data available on the reference reactions in order to develop a transition state model of reaction 1,-1.



Figure 5. Plot of experimental and calculated values of k^{∞_1} vs 1000/ *T*: open circles, Lin and Laidler (ref 17); heavy line, Gruver and Calvert (refs 15 and 16). Narrow line is obtained from the TST calculations using the model described in text, section III.3. Dashed lines represent the k^{∞_1} values obtained with the energy barrier height for decomposition, ΔE_1 , changed by ± 2 kJ mol⁻¹.

Decomposition Reaction sec- $C_4H_9 \rightarrow CH_3 + C_3H_6$ (1). Gierczak et al.¹⁸ studied chemically activated s- C_4H_9 from the photolysis of H₂S/*cis*-2-butene mixtures with final product analysis. Kinetic modeling was used to determine the rates of unimolecular decomposition and isomerization of the *sec*-butyl radical. No details of the model are reported, and it is not clear to what extent the results ($A = 10^{13.56} \text{ s}^{-1}$, threshold energy = 133.3 kJ mol⁻¹) are affected by the assumptions and details of the model. We therefore do not consider the results of Gierczak et al.¹⁸ in creating our transition state model.

Gruver and Calvert^{15,16} and Lin and Laidler¹⁷ determined the decomposition rate constant relative to that of the recombination reaction (5).

$$sec-C_{4}H_{9} + sec-C_{4}H_{9} \rightarrow CH_{3}CH_{2}CH(CH_{3})CH_{2}CH_{3}(5)$$

Gruver and Calvert¹⁵ photolyzed 2-methylbutanal at 313 nm as a *sec*-C₄H₉ source. The experiments were conducted at an average pressure of 46 Torr of 2-methylbutanal using final product analysis. Their results were reanalyzed by Calvert¹⁶ to yield the expression $k_1/k_5^{1/2} = 1.11 \times 10^{19} \exp(-15399 \text{ K/T})$ molecule^{1/2} cm^{-3/2} s^{-1/2} in the temperature range 516–622 K. Lin and Laidler studied the azomethane-sensitized decomposition of *n*-butane with gas chromatography at T = 536-613 K and pressures of *n*-butane of 59–204 Torr. The results give $k_1/k_5^{1/2} = 1.02 \times 10^{20} \exp(-16405 \text{ K/T})$ molecule^{1/2} cm^{-3/2} s^{-1/2}. The temperature ranges of these two studies almost coincide, and the results can be compared directly. The results of Lin and Laidler are, on average, 60% higher than those of Gruver and Calvert between 536 and 613 K and have a higher activation energy.

In order to obtain k^{∞_1} values from the above relative measurements, knowledge of the rate constant for the recombination of *sec*-butyl radicals, k_5 , is required. No experimental data are available on this reaction. Following the suggestions of Tsang⁶ and Marshall,²⁷ one can assume that k_5 equals the rate constant of the recombination of isopropyl radicals. Taking the recommendation of Tsang²⁸ for the latter value, we obtain $k_5 = 1 \times 10^{-11} (300/T)^{0.7}$ cm³ molecule⁻¹ s⁻¹. Using this expression and results of Lin and Laidler¹⁷ and of Gruver and Calvert,^{15,16} values of k_1 are obtained which can be fitted with

simple Arrhenius expressions in the experimental temperature ranges of these authors. We obtain

$$v_1(\text{GC}) = 2.00 \times 10^{13} \exp(-15205 \text{ K/T}) \text{ s}^{-1}$$
 (I)

from the results of Gruver and Calvert and

k

$$k_1(LL) = 2.03 \times 10^{14} \exp(-16265 \text{ K/T}) \text{ s}^{-1}$$
 (II)

from the results of Lin and Laidler (Figure 5).

Association (Reverse) Reaction $CH_3 + C_3H_6 \rightarrow sec-C_4H_9$ (-1). Miyoshi and Brinton¹⁹ studied the pyrolysis of di-*tert*butyl peroxide in the presence of propylene with product analysis by gas chromatography and mass spectrometry. They determined the overall rate constant of the CH₃ addition to propylene

$$CH_3 + C_3H_6 \rightarrow C_4H_9 \qquad (-1')$$

but did not distinguish between the routes forming sec-butyl radicals (reaction -1) and isobutyl radicals. Values of the overall rate constant, k'_{-1} , at T = 381-441 K and $[C_8H_{18}O_2] = (0.3-3) \times 10^{17}$ molecules cm⁻³ were obtained relative to methyl radical recombination,

$$2CH_3 \rightarrow C_2H_6 \tag{6}$$

It was observed by Baldwin et al.²² that the temperature dependence of the $k'_{-1}/k_6^{1/2}$ values reported by Miyoshi and Brinton has the wrong preexponential factor. (This error propagated into the recommendation of Kerr and Parsonage²⁹ for the rate constant of reaction -1' which was based on the expression of Miyoshi and Brinton.) We calculated the values of k'_{-1} using the individual values of $k'_{-1}/k_6^{1/2}$ reported by Miyoshi and Brinton and k_6 obtained from the parametrization of Walter et al.³⁰ (recommended for Ar) with correction for ditert-butyl peroxide as bath gas. In this correction the collision frequency was calculated using the Lennard-Jones parameters of di-tert-butyl peroxide estimated from the boiling point and additive volume increments.³¹ $\langle \Delta E \rangle_{down}$ for the di-*tert*-butyl peroxide (to which the rate constants are relatively insensitive close to the high-pressure limit) was assumed to equal 1000 cm^{-1} . Reaction 6 is in the falloff region at the conditions of experiments of Miyoshi and Brinton, although close to the highpressure limit. (The average value of k_6/k_6^{∞} is 0.86.)

Cvetanovic and Irwin²⁰ studied the overall reaction -1' using the photolysis of biacetyl and acetone as a source of CH₃ radicals. The ratio of the rate constants of the reactions of methyl radicals with propene (addition) and with isobutane (abstraction) was determined from analysis of CO and CH₄ yields at T = 353-453 K and 3000 Torr. The literature data on the rate constant of the latter reaction

$$CH_3 + i - C_4 H_{10} \rightarrow CH_4 + C_4 H_9 \tag{7}$$

were analyzed recently by Zhang and Back,³² who recommend $k_7 = 6.61 \times 10^{-13} \exp(-4510 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. We used this expression to obtain the values of k'_{-1} from the results of Cvetanovic and Irwin.

Tedder et al.²¹ investigated the terminal addition of the CH₃ radicals to propene, reaction -1. The reaction was studied using the competitive rates technique in a high-pressure reactor, with photolysis of azomethane as a source of methyl radicals and chromatographic analysis of products. The temperature range of this study was 335-424 K. Taking the rate constants for the addition of CH₃ to ethylene (the reference reaction in the experiments of Tedder et al.) from Holt and Kerr,³³ we obtain values of k_{-1} shown in Figure 6.



Figure 6. Plot of experimental and calculated values of k^{∞}_{-1} vs 1000/ *T*: Miyoshi and Brinton (ref 19), Cvetanovic and Irwin (ref 20), Baldwin et al. (ref 22), Tedder et al. (ref 21). Line is obtained from the TST calculations using the model described in text, section III.3.

Baldwin et al.²² determined the rate constant of the addition (terminal and nonterminal) of CH_3 to propene relative to the reaction of methyl radicals with molecular hydrogen

$$CH_3 + H_2 \rightarrow CH_4 + H \tag{8}$$

at 753 K and a pressure of ≈ 500 Torr. The value $k_{-1}/k_8 =$ 3.84 was obtained from an analysis of the yields of isomers of butene and methane resulting from the addition of propene to a slowly reacting mixture of H₂ and O₂. To obtain the value of k_{-1} , knowledge of the rate constant of the reference reaction 8 is required. Recommendations of several sources^{1,4,34,35} at T = 753 K differ as much as by a factor of 2. We used the lowest⁴ ($k_8 = 1.35 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹) and the highest¹ ($k_8 =$ 2.65 $\times 10^{-15}$ cm³ molecule⁻¹ s⁻¹) values of the above recommendations to obtain $k_{-1} = 5.18 \times 10^{-15}$ and $k_{-1} = 1.02 \times 10^{-14}$ from the results of Baldwin et al. These two limiting values are displayed in Figure 6.

The experimental studies of Miyoshi and Brinton¹⁹ and of Cvetanovic and Irwin²⁰ did not distinguish between terminal and nonterminal addition of CH₃ to propene. Following the recommendation of Baldwin et al. $(k_{-1}/k'_{-1} = 0.58 \text{ exp}(176 \text{ K/T})$ to calculate the values of k_{-1} from the results of ref 19 and ref 20. The values of k_{-1} obtained from this analysis of the four studies of reaction -1 are displayed in Figure 6. The results of Miyoshi and Brinton¹⁹ and Cvetanovic and Irwin²⁰ are in excellent agreement. Together they give

$$k_{-1}^{\infty} = 1.81 \times 10^{-12} \exp(-4239 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (III)

at T = 353-453 K. The rate constants based on the results of Baldwin et al.²² are in approximate agreement with expression III. However, they were not used at this stage to determine $k^{\infty}_{-1}(T)$ because of the large uncertainty in the reference reaction and because reaction -1 is not precisely in the high-pressure limit under the conditions of the experiments of Baldwin et al. (vide infra). The results of Tedder et al.²¹ are lower than values obtained from formula III by a factor of 10 and exhibit a lower activation energy. Due to this large discrepancy between the results of Tedder et al. and other studies, ^{19,20,22} the former are excluded from the further analysis.

TABLE 2:	Molecular	Parameters	of the	Transition	State
(sec-C ₄ H ₉ [‡])					

barrier for dece	Some point of the end	30.46 kJ mol ⁻¹ 32.4 kJ mol ⁻¹
2950 (4), 2860 (800, 600 (2),	vibrational frequencies (cm ⁻¹) 5), 1470 (5), 1400 (3), 1300, 110 450, 350, 240 (2), 190	0, 1000, 900 (2),
rotational	constants (cm ⁻¹), symmetry nun	nbers, and
	rotational barriers (kJ mol ⁻¹)	
overall rotation	$A = 0.481; \sigma = 1$ (active)	
	$(BC)^{1/2} = 0.146; \sigma = 1$ (inactional distance)	ive)
internal rotations	$a_1(CH_3-CH_2CHCH_3) = 5.61;$	$\sigma = 3; V_0 = 0$
	$a_2(CH_3CH_2CH-CH_3) = 5.62;$	$\sigma = 3; V_0 = 6.0$
	Lennard-Jones parameters ^a	
	$(I_{\rm L}(V))$	~ (Å)

gas	ϵ/k (K)	σ (Å)
He	10.22	2.551
Ar	93.3	3.542
N_2	71.4	3.798
sec-C ₄ H ₉ ^b	531.4	4.687

^a From ref 31. ^b Taken to be the same as for n-C₄H₁₀.

2. Transition State Model of Reaction 1,-1. The development of a transition state model for reaction 1,-1 was based on expression III for the temperature dependence of the rate constant of reaction -1. The coincidence of the results of two studies^{19,20} of this reaction and the approximate agreement of the results of Baldwin et al.²² with them strongly support this choice.

Calculation of k^{∞}_1 and k^{∞}_{-1} requires knowledge of the structure and vibrational frequencies of the involved molecules. The geometric structure and vibrational frequencies of the methyl radical and propene as well as the barrier for the internal rotation in the propene molecule are known.^{36,37} The model of the sec-C₄H₉ radical was taken from the results of the ab initio study of Chen et al.³⁸ The barrier for the C_2-C_3 internal rotation in the sec-butyl radical was taken as 9.04 kJ mol⁻¹, which results from the ab initio calculations. (The correction³⁸ to the original article of Chen et al. contains the value of 4.6 kJ mol⁻¹, which is a misprint.) All hindered rotations were treated classically³⁹ in order to maintain compatibility with classical expressions for the density-of-states and sum-of-states functions of a hindered internal rotor14 which are required for later calculation of energyspecific rate constants, k(E). The errors in the values of rate contants due to this classical approach are less than 1% for k^{∞}_{-1} and less than 4% for k^{∞}_1 at temperatures higher than 298 K, as determined by comparing classical partition functions with exact tabulated values.39

 k^{∞}_{-1} is given by⁴⁰

$$k_{-1}^{\infty} = \frac{k_{\rm B}T}{h} \frac{Q^{\ddagger}}{Q_{\rm CH_3}Q_{\rm C_3H_6}} \exp\left(-\frac{\Delta E_{-1}}{k_{\rm B}T}\right)$$

where Q^{\ddagger} , Q_{CH_3} , and $Q_{C_3H_6}$ are partition functions of the transition state, CH₃ radical, and propene molecule, respectively, and ΔE_{-1} is the energy barrier height for association. There exists an addition barrier in reaction -1, and hence, the transition state is tight. The moments of inertia of the transition state were taken as equal to those of conformation VI of the *sec*-butyl radical in the study of Chen et al.³⁸ (that most resembling the configuration of the transition state and the addition energy barrier height for the association reaction ΔE_{-1} were varied to fit Arrhenius expression III at temperatures in the range 353–453 K. Frequencies and other parameters of the transition state obtained through this fitting procedure are listed in Table 2.

Since hindered internal rotations in $sec-C_4H_9$, propene, CH_3 , and the transition state are treated classically, the energies of these rotations are calculated relative to the minimum of the potential energy of the torsional motion.

The barrier to dissociation of the *sec*-C₄H₉ radical was obtained from the master equation/RRKM fitting of our experimental data (section III.3). The *sec*-butyl radical has no optical isomers, no overall rotational symmetry, and two internal methyl rotors with symmetry factors of 3 each—total symmetry factor 9. The transition state has the same rotational symmetry. Taking into account the existence of two optical isomers in the transition state, we obtain⁴⁰ the reaction path degeneracy of 2 for the decomposition reaction.

The model of the transition state described above results in the following expression for high-pressure limit rate constant of reaction -1 at T = 298-1500 K:

$$k_{-1}^{\infty} = 2.13 \times 10^{-19} T^{2.28} \exp(-3319 \text{ K/T})$$

 cm^3 molecule⁻¹ s⁻¹ (IV)

which is plotted in Figure 6 together with the experimental determinations.

3. Master Equation Calculations of $k_1(T, [M])$ and Determinations of the Energy Barrier for Decomposition and $\langle \Delta E \rangle_{down}$. The measured rate constants of reaction 1 ($k_1(T, [M])$) were reproduced using master equation simulations. The "exponential-down" model⁴⁰⁻⁴² of collisional energy transfer was adopted to characterize the probability of deactivation of the *sec*-C₄H₉ molecule with a total internal energy *E* in active degrees of freedom to a final energy *E'* by collision with a molecule of bath gas:

$$P(E',E) = A \exp(-[E - E']/\langle \Delta E \rangle_{\text{down}}), \quad E' \le E \quad (V)$$

 $\langle \Delta E \rangle_{\text{down}}$ is the average energy lost in deactivating collisions, and A is a normalization constant. The energy-dependent rate constants k(E) were calculated using the RRKM method.^{40,43} The density-of-states and sum-of-states functions of the *sec*butyl radical and the transition state, needed for the calculation of k(E) values and further analysis, are obtained from the models of these species described above. Hindered internal rotors were treated classically using the simple formalism introduced by us earlier.¹⁴ The density-of-states function was calculated separately for each hindered internal rotor of the *sec*-C₄H₉ radical. The total rotational density-of-states function was calculated by numerical convolution of these individual functions. The density-of-states of vibrational degrees of freedom was included using the modified Beyer–Swinehart algorithm.⁴⁴ The sumof-states function for the transition state was similarly calculated.

The method of Gaynor et al.^{40,45} for solving the master equation was employed. The energy bin size used in the fitting procedures was $20-40 \text{ cm}^{-1}$. By comparing the exact values of the partition functions and high-pressure-limit rate constants with those obtained by numerical integration, it was found that errors resulting from numerical convolution of the density-ofstates and sum-of-states functions, as well as from numerical integration, are not more than 6% of the exact values at the temperatures of the experiments.

The optimum value of the energy barrier for the decomposition, ΔE_1 , was obtained using a grid search with a step size of 1 kJ mol⁻¹. With each fixed value of ΔE_1 a weighted sum of squares of deviations between calculated and experimental rate constants was minimized using $\langle \Delta E \rangle_{\text{down}}$ as an adjustable parameter. Each data point was assigned a weight of $1/k_1$. The optimized values of this weighted sum of squares of deviations were obtained as a function of ΔE_1 and fitted with a parabolic function in the vicinity of the minimum. This procedure was repeated for each bath gas (He, Ar, and N₂) assuming two

TABLE 3: Optimized Values of the Energy Barrier Height ΔE_1 and $\langle \Delta E \rangle_{down}$ of Reaction 1 from the Master Equation Modeling (Section III.3)

bath gas	$\Delta E_1/kJ \text{ mol}^{-1}$	$\langle \Delta E \rangle_{down}/cm^{-1}$
	Assuming $\langle \Delta E \rangle_{\text{down}} =$	α <i>T</i>
He	130.46	0.531T
Ar	131.60	0.952T
N_2	129.37	0.598T
Assu	ming $\langle \Delta E angle_{ m down}$ Independen	t of Temperature
He	130.91	382
Ar	131.98	671
N_2	129.96	433

models of the temperature dependence of $\langle \Delta E \rangle_{\rm down}$. First, $\langle \Delta E \rangle_{\rm down}$ was taken as independent of temperature, $\langle \Delta E \rangle_{\rm down} =$ constant. Second, it was assumed to be directly proportional to temperature, $\langle \Delta E \rangle_{\rm down} = \alpha T$. The latter model is based on our earlier studies of the reaction

$$C_2H_5 \rightleftharpoons H + C_2H_4 \tag{9}$$

Our analysis of this system⁹ demonstrated a strong dependence of $\langle \Delta E \rangle_{down}$ on temperature, increasing from 70–100 cm⁻¹ at 300 K to 280 cm⁻¹ at 1100 K. This dependence was best fit with the directly proportional dependence, $\langle \Delta E \rangle_{down} = 0.255T$ cm⁻¹. The analysis of the *i*-C₃H₇ \rightleftharpoons H + C₃H₆ system¹⁰ also supports a strong temperature dependence of $\langle \Delta E \rangle_{down}$ for He as bath gas.

The resultant optimized values of ΔE_1 obtained with both models of the temperature dependence of $\langle \Delta E \rangle_{\rm down}$ from the analysis of the experimental data are listed in Table 3 for the three bath gases used. Reaction 1 is close to the high-pressure limit under the conditions of our experiments $(k_1([M],T)/k^{\infty}) =$ 0.11-0.48 if the model with $\Delta E_1 = 130.46 \text{ kJ mol}^{-1}$ is used), and hence, the calculated values of the rate constant are relatively insensitive to $\langle \Delta E \rangle_{\text{down}}$ and, consequently, to its temperature dependence. As can be seen from Table 3, the difference between the values of ΔE_1 obtained with the two models of the temperature dependence of $\langle \Delta E \rangle_{\text{down}}$ is only 0.5 kJ mol⁻¹. At the same time, the difference between values obtained from fitting of the data for Ar and N₂ as bath gas is 2.2 kJ mol⁻¹. In general, the agreement between results for He, Ar, and N₂ is good. We select for further use in our model of reaction 1,-1 (Table 2) the value of $\Delta E_1 = 130.46$ kJ mol⁻¹, which is the average of the results for three bath gases obtained assuming $\langle \Delta E \rangle_{down}$ directly proportional to temperature. From the difference between individual values of the energy barrier for the decomposition of $sec-C_4H_9$ in Table 3, we estimate the uncertainty in ΔE_1 as $\pm 2 \text{ kJ mol}^{-1}$.

This model of reaction 1,-1 results in the following expression for the high-pressure-limit rate constant of the *sec*-butyl radical decomposition at T = 298-1500 K:

$$k_{1}^{\infty} = 2.73 \times 10^{10} T^{1.11} \exp(-15712 \text{ K/T}) \text{ s}^{-1}$$

which is plotted in Figure 5 together with the experimental determinations of refs 15-17.

The "global" fitting (described above) of the experimental data using the selected model of reaction 1,-1 and the assumption of $\langle \Delta E \rangle_{\text{down}} = \alpha T$ results in the following values of the coefficient α :

$$\langle \Delta E \rangle_{\text{down}} = 0.531T \,\text{cm}^{-1}$$
 for He as bath gas (VIa)

$$\langle \Delta E \rangle_{\text{down}} = 0.720T \,\text{cm}^{-1}$$
 for Ar as bath gas (VIb)

$$\langle \Delta E \rangle_{\text{down}} = 0.742T \,\text{cm}^{-1}$$
 for N₂ as bath gas (VIc)



Figure 7. "Reduced" function $\langle \Delta E \rangle_{down}/(\alpha T)$ vs pressure for three bath gases (see text, section III.3). The plot shows an absence of any pressure dependence which means that the model describes all sections of falloff equally well in the experimental pressure range.

The values of the rate constants $k_1([M],T)$ calculated using the accepted model of the reaction (Table 2) and formulas VIa–VIc are presented in Figures 1 and 2 together with the experimental data.

Individual values of $\langle \Delta E \rangle_{\rm down}$ can be obtained for each experiment listed in Table 1 by reproducing the experimental values of rate constants with the solution of the master equation using $\langle \Delta E \rangle_{\rm down}$ as an adjustable parameter. Such calculations were performed with the selected model of the reaction. The resultant values of $\langle \Delta E \rangle_{\rm down}$ are listed in Table 1. The average values of $\langle \Delta E \rangle_{\rm down}$ for the three bath gases used are consistent (as expected) with expressions VIa–VIc: 363 (He), 447 (Ar), and 506 cm⁻¹ (N₂). Due to the scatter of individual values, no information on the temperature dependence of $\langle \Delta E \rangle_{\rm down}$ can be extracted from these results.

A check of the quality of the model and data analysis procedure is provided by an inspection of the pressure dependence of $\langle \Delta E \rangle_{down}$. The fitted values of $\langle \Delta E \rangle_{down}$ should exhibit no dependence on pressure. To isolate the pressure dependence from the temperature dependence, a "reduced" function $\langle \Delta E \rangle_{down} / (\alpha T \text{ cm}^{-1})$ is used with the values of α taken from formulas VIa–VIc. The values of function vs pressure are plotted in Figure 7. The plot shows the absence of any pressure dependence which indicates that the model describes all sections of falloff in helium, argon, and nitrogen equally well in the experimental pressure range. In addition, if the values of $\langle \Delta E \rangle_{down}$ itself are plotted vs pressure, no dependence can be seen.

4. Analysis of Prior Experimental Studies of Reaction 1,-1. Among the experimental determinations of k_{-1} , those of Miyoshi and Brinton¹⁹ and Cvetanovic and Irwin²⁰ were performed at the conditions of the high-pressure limit. The experimental study of reaction -1 by Baldwin et al.²² was conducted at 753 K and a total pressure of 500 Torr of a mixture of N₂, O₂, H₂, and C₃H₆. The composition of the mixture was varied in different experiments, with N₂, O₂, or H₂ being in excess. We calculated the k_{-1}/k^{∞}_{-1} ratio for the conditions of these experiments using the collisional parameters of N₂ for the bath gas and our accepted model of reaction 1,-1. The high-pressure-limit rate constant value resulting from our model

is $k^{\infty}_{-1} = 9.0 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹. If $\langle \Delta E \rangle_{down} = 559$ cm⁻¹ (from formula VIc) is used, then $k_{-1}/k^{\infty}_{-1} = 0.66$ and $k_{-1} = 6.0 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹. Using a value of $\langle \Delta E \rangle_{down} 2$ times lower results in a decrease of k_{-1} by only 26% ($k_{-1} = 4.4 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹). The error limits of the experimental value caused by the uncertainty in the rate constant of reaction 8 (the reference reaction in the experiments of Baldwin et al.) are higher (section III.1) than the possible variation of the k_{-1}/k^{∞}_{-1} ratio. Use of different recommendations for k_8 yields the values of k_{-1} in the range (5.2–10.2) $\times 10^{-15}$ cm³ molecule⁻¹ s⁻¹. Hence, no information on falloff effects can be extracted from these experimental data, although an approximate agreement between the experimental and calculated values is attained (Figure 6).

The modeling of the results of Lin and Laidler¹⁷ and Gruver and Calvert^{15,16} indicates that they were obtained at conditions nearly at the high-pressure limit of reaction 1. If $\langle \Delta E \rangle_{\text{down}} =$ 1000 cm⁻¹ is used for the large polyatomic bath gases $(2-methylbutanal^{15} and n-butane^{17})$ used in these studies, we obtain k_1/k^{∞_1} values of 0.8-0.9 for the conditions of the experiments of Gruver and Calvert and 0.8-1.0 for the conditions of Lin and Laidler. In both studies the ratio of k^{∞} ₁/ $k_5^{1/2}$ was determined. Taking k_5 as equal to the rate constant of the recombination of isopropyl radicals, one obtains the values discussed in section III.1 (formulas I and II) and plotted in Figure 5. These results are considerably higher than $k^{\infty}_{1}(T)$ obtained from our model of reaction 1, -1. The difference is as high as a factor of 2.5 (Lin and Laidler) and 1.6 (Gruver and Calvert). The $\pm 2 \text{ kJ mol}^{-1}$ uncertainty in the barrier for the decomposition of sec-C₄H₉ radicals (section III.3) results in a change in k^{∞}_1 at T = 580 K (average temperature of these two relative studies) of a factor of 1.5. The authors of refs 15-17did not report experimental uncertainties of the determinations of $k_1/k_5^{1/2}$, but they can be estimated from the difference between the results of these two studies-a factor of 1.6. This value combined with the factor of 1.4 obtained from the square root of the uncertainty in the isopropyl radical recombination rate constant²⁸ results in a factor of 2.1 for overall uncertainty in the experimental data in Figure 5. Thus, estimated uncertainty limits of the experimental data and those of $k^{\infty}(T)$ from our model overlap.

IV. Discussion

1. Thermochemistry of the sec-C₄H₉ Radical. Kinetic information on reactions 1 and -1 can be used to obtain the enthalpy of reaction and, through this, the enthalpy of formation of the sec-butyl radical. The recommended value of $\Delta E_1 =$ $130.46 \pm 2.0 \text{ kJ mol}^{-1}$ together with the fitted value of the barrier for the reverse reaction, $\Delta E_{-1} = 32.4$ kJ mol⁻¹, gives the energy difference between reactants and products of reaction 1,-1, $\Delta E_{1,-1} = 98.07$ kJ mol⁻¹. Using the models described above of sec-C₄H₉, CH₃, and C₃H₆ and taking into account the zero-point energies of the torsional rotations (excluded from ΔE_1 and ΔE_{-1}), one can obtain for the enthalpy of the reaction $1,-1 \Delta H^{\circ}_{298} = 101.05 \text{ kJ mol}^{-1}$. With $\Delta H_{f}^{\circ}_{298}(CH_3) = 146.0$ \pm 1.0 kJ mol⁻¹ (refs 46 and 47) and $\Delta H_{f}^{\circ}_{298}(C_{3}H_{6}) = 20.0 \pm$ 0.8 kJ mol⁻¹ (ref 48), we obtain $\Delta H_{f^{\circ}298}(sec-C_{4}H_{9}) = 65.0$ kJ mol^{-1} . The uncertainty of this value can be estimated from the combined uncertainties in the heats of formation of CH₃ and C_3H_6 and the error limits of the enthalpy of reaction 1,-1, ± 2.5 kJ mol⁻¹. The latter value is estimated as twice the change of enthalpy obtained if different recommendations are used for the rate constant of reaction 7. (The reference reaction in the study of Cvetanovic and Irwin²⁰.) If the recommendation of Tsang⁴⁹ is used instead of that of Zhang and Back,³² the values of k_{-1} from ref 20 become 30% lower and the activation energy of reaction -1 obtained from ref 19 (unaffected by this change) and ref 20 reduces. The resultant formula is $k^{\infty}_{-1} = 9.16 \times 10^{-13} \exp(-4022 \text{ K/T}) \text{ cm}^3$ molecule⁻¹ s⁻¹ instead of expression III. If a new transition state model is created to reproduce this equation, and the master equation fitting process described in section III.3 is repeated with this new model, it results in a change of the enthalpy of reaction 1,-1 by -1.25 kJ mol⁻¹. The resultant uncertainty in the $\Delta H_{\rm f}^{\circ}_{298}(sec-C_4H_9)$ value is ± 3.4 kJ mol⁻¹.

Tsang⁶ used the available literature data¹⁵⁻¹⁷ on reaction 1 together with the temperature dependence of k^{∞}_{-1} recommended by Kerr and Parsonage²⁹ to obtain $\Delta H_{\rm f}^{\circ}_{298}(sec\text{-}C_4\text{H}_9) = 71.0$ kJ mol⁻¹. The difference between Tsang's value and that reported herein is due mainly to the different temperature dependencies of k^{∞}_{-1} and k^{∞}_{-1} used in the two investigations.

Our $\Delta H_{f^{\circ}298}^{\circ}(sec-C_4H_9) = 65.0 \pm 3.4 \text{ kJ mol}^{-1}$ is 2.5 kJ mol⁻¹ lower than the most recent and directly determined value of Seakins et al.⁵⁰ (67.5 ± 2.3 kJ mol⁻¹ from the third law treatment and 67.6 ± 3.0 from the second law treatment of the results on the kinetics of $sec-C_4H_9 + \text{HBr} \rightleftharpoons n-C_4H_{10} + \text{Br}$ reaction). This disagreement lies within error limits of both studies and is not large considering the indirect nature of the value obtained in the current study which relies on the results of relative rate constant determinations.

2. Uncertainty in the $\langle \Delta E \rangle_{\text{down}}$ Determination in Reaction 1,-1. There are sources of uncertainty in the model of reaction 1,-1 which propagate into possible errors in the determination of $\langle \Delta E \rangle_{\text{down}}$. Since reaction 1,-1 is relatively close to its highpressure limit at the conditions of these experiments, small variation of the calculated values of k^{∞_1} at these temperatures will noticeably affect the fitting parameters (i.e., the determinations of $\langle \Delta E \rangle_{\text{down}}$). In this section we explore the propagation of these uncertainties, first in calculating k^{∞}_{1} (from k^{∞}_{-1} obtained from experiment) and then in $\langle \Delta E \rangle_{down}$. In the error assessment, first the influence of the ± 2.0 kJ mol⁻¹ uncertainty in the barrier for the sec-C₄H₉ decomposition on the fitted values of $\langle \Delta E \rangle_{down}$ is investigated. Then the model of reaction 1,-1 is modified by using the energy barrier height for the sec-butyl radical decomposition obtained from the value of $\Delta H_{f^{\circ}298}(sec-C_{4}H_{9})$ reported by Seakins et al., and the effect of this model change is examined.

The master equation fitting exercise described above was repeated with no changes of the structure and frequencies of the transition state, but with the barrier height for decomposition changed by $\pm 2.0 \text{ kJ mol}^{-1}$. This provided a change of k^{∞}_1 at 640 K, the average temperature of our experiments, of a factor of 1.45. The resulting individual calculated values of $\langle \Delta E \rangle_{\text{down}}$ are significantly affected by these variations of the model. The fitted values of $\langle \Delta E \rangle_{\text{down}}$ are 673/240 (He), 774/302 (Ar), and 970/331 cm⁻¹ (N₂) with the lower values corresponding to the lower value of the energy barrier.

These results can be considered as upper and lower limits of the $\langle \Delta E \rangle_{\text{down}}$ parameter obtained from the analysis of our experimental data. Hence, we obtain

$$\langle \Delta E \rangle_{\text{down}} = 363^{+310}_{-123} \text{ cm}^{-1}$$
 for He as bath gas
 $\langle \Delta E \rangle_{\text{down}} = 447^{+327}_{-145} \text{ cm}^{-1}$ for Ar as bath gas
 $\langle \Delta E \rangle_{\text{down}} = 506^{+464}_{-175} \text{ cm}^{-1}$ for N₂ as bath gas

If the value of $\Delta H_{\rm f}^{\circ}_{298}(sec-C_4H_9) = 67.5 \text{ kJ mol}^{-1}$ reported by Seakins et al.⁵⁰ is used together with literature data^{46–48} on the enthalpy of formation of CH₃ and C₃H₆ to calculate ΔE_1 (with structure and frequencies of the transition state obtained from the kinetic information on reaction -1 unchanged), the value of $\Delta E_1 = 127.9 \text{ kJ mol}^{-1}$ is obtained. This is 2.5 kJ mol⁻¹ lower than the value used in the model described above. Such a variation of ΔE_1 significantly changes the fitting results. The average values of $\langle \Delta E \rangle_{\text{down}}$ in this case are 218 (He), 275 (Ar), and 301 cm⁻¹ (N₂). In this case the individual fitted values of $\langle \Delta E \rangle_{down}$ show a pronounced dependence on pressure. The average values of $\langle \Delta E \rangle_{\rm down}$ obtained at [He] = 3 $\times 10^{16}$ molecules cm^{-3} are 30% higher than those obtained at [He] = 18×10^{16} molecules cm⁻³, with similar dependencies obtained for Ar and N₂ as bath gas. Such a dependence indicates a poor quality of fit, and hence, this value of ΔE_1 is unrealistic.

The average values of the $\langle \Delta E \rangle_{\text{down}}$ parameter obtained for the three bath gases used in the current study are considerably higher than what can be expected based on values for other alkyl radicals which have now been determined (250 cm^{-1} for C_2H_5 , 220 cm⁻¹ for *n*- C_3H_7 , 11 136–210 cm⁻¹ for *i*- C_3H_7 , 10 140-280 cm⁻¹ for CH₃CO,¹² 255 cm⁻¹ for CH₃CHCl,¹³ 300 cm^{-1} for neo-C₅H₁₁,⁵¹ and 230 cm⁻¹ for t-C₄H₉¹⁴ with He as bath gas). This difference may be caused by uncertainties in the high-pressure-limit rate constant and in the thermochemistry of the reaction as described above. The change of the decomposition barrier height by -2.0 kJ mol^{-1} reduces the average fitted values of $\langle \Delta E \rangle_{\text{down}}$ but results in a poorer agreement between the experimental and calculated rate constants. Another possible explanation for the high values of $\langle \Delta E \rangle_{\text{down}}$ is an underestimation of the density-of-states function caused by the assumptions of harmonic vibrational potential and sinusoidal potential of hindered internal rotations.

V. Parametrization of Rate Constants

We present here a parametrization of k_1 in helium, argon, and nitrogen which provides rate constant values throughout the range of temperatures 298–1500 K and pressures 0.001– 10 atm. The modified Lindemann-Hinshelwood expression introduced by Gilbert et al.⁵² was used:

$$\frac{k_1}{k_1^{\infty}} = \frac{k_1^0[M]/k_1^{\infty}}{1 + k_1^0[M]/k_1^{\infty}} F(F_{\text{cent}},[M])$$
(VII)

Values of $k_1([\mathbf{M}],T)$ in the above temperature and pressure intervals were calculated using the master equation/RRKM approach assuming the directly proportional temperature dependencies of $\langle \Delta E \rangle_{down}$ for all three bath gases with the coefficients obtained from the modeling of experimental data (VIa-VIc). The matrix of calculated values of $k_1([\mathbf{M}],T)$ was fitted with the modified Lindemann-Hinshelwood expression VII, and the resulting parameters are

$$k_{1}^{\infty} = 2.73 \times 10^{10} T^{1.11} \exp(-15712 \text{ K/T}) \text{ s}^{-1}$$

and

$$k_{1}^{0} = 2.76 \times 10^{29} T^{-10.9} \exp(-17971 \text{ K/T})$$

cm³ molecule⁻¹ s⁻¹

 $F_{\text{cent}} = 0.438 \exp(-T/882 \text{ K}) + 20.4 \exp(-7243 \text{ K/T})$

for helium as bath gas

$$k_{1}^{0} = 2.43 \times 10^{28} T^{-10.6} \exp(-17638 \text{ K/T})$$

cm³ molecule⁻¹ s⁻¹

$$F_{\text{cent}} = 0.369 \exp(-T/946 \text{ K}) + 24.8 \exp(-7639 \text{ K/T})$$

for argon as bath gas

$$k_{1}^{0} = 1.65 \times 10^{28} T^{-10.5} \exp(-17607 \text{ K/T})$$

 $\text{cm}^{3} \text{ molecule}^{-1} \text{ s}^{-1}$
 $F_{\text{cent}} = 0.371 \exp(-T/950 \text{ K}) + 23.9 \exp(-7616 \text{ K/T})$

for nitrogen as bath gas.

The average deviation of the parametrized values of k_1 from the master equation rate constants over this large range of conditions is 5%, with maximum deviation of 35%.

Due to the uncertainty in the parameters of the model discussed above and in the temperature dependence of $\langle \Delta E \rangle_{down}$, caution is advised in using the results of this extrapolation far outside the temperature range of the current study.

VI. Summary

The unimolecular decomposition of sec-C₄H₉ in helium, argon, and nitrogen has been studied in the falloff region. A transition state model of reaction 1, -1 was developed which provides the high-pressure-limit rate constants. The model was used to provide k(E) values for the master equation analysis. The experimental values of k_1 were reproduced by master equation/RRKM modeling. Finally, parametrized expressions are presented which provide values of k_1 over a wide range of pressures and temperatures.

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