## Unimolecular Decomposition of *n*-C<sub>4</sub>H<sub>9</sub> and *iso*-C<sub>4</sub>H<sub>9</sub> Radicals

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The kinetics of the unimolecular decomposition of the  $n-C_4H_9$  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 (560-620 K) and bath gas density  $((3-18) \times 10^{16} \text{ molecules cm}^{-3})$  in two bath gases, He and N<sub>2</sub>. The rate constants are in the falloff region under the conditions of the experiments. Structures, vibrational frequencies, and barriers for internal rotations of *n*-butyl and *iso*-butyl radicals and their decomposition transition states were obtained by ab initio calculations using UHF/6-31G\* and MP2/6-31G\* methods. The results of ab initio calculation, together with the reanalysis of earlier studies of the reverse reactions, were used to create transition-state models of the reactions of unimolecular decomposition of n-butyl (1) and iso-butyl (2) radicals. Falloff behavior of reaction 1 was reproduced using master equation modeling with the energy barrier height for decomposition obtained from optimization of the agreement between experimental and calculated rate constants. The values of  $\langle \Delta E \rangle_{all} = -28 \text{ cm}^{-1}$  (He) and  $-40 \text{ cm}^{-1}$  (N<sub>2</sub>) for the average energy loss per collision were obtained using an exponential-down model. The resulting models of the reactions provide the high-pressure limit rate constants for the decomposition reactions  $(k_1^{\infty}(n-C_4H_9 \rightarrow C_2H_5 + C_2H_4) = 1.06 \times 10^{13} \exp(-14005)$ K/T),  $k_2^{\infty}(iso-C_4H_9 \rightarrow CH_3 + C_3H_6) = 2.14 \times 10^{12}T^{0.65} \exp(-15529 \text{ K/T}) \text{ s}^{-1}$  and the reverse reactions  $(k_{-1}^{\infty}(C_2H_5 + C_2H_4 \rightarrow n-C_4H_9) = 6.59 \times 10^{-21}T^{2.44} \exp(-2697 \text{ K/T}), k_{-2}^{\infty}(CH_3 + C_3H_6 \rightarrow iso-C_4H_9) = 1.66$  $\times 10^{-20}T^{2.57} \exp(-3879 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ). Parametrization of the temperature and pressure dependence of the unimolecular rate constants for the temperature range 298–900 K and pressures 0.001–10 atm in He and N<sub>2</sub> is provided using the modified Lindemann-Hinshelwood expression.

### I. Introduction

The unimolecular decomposition of molecules and polyatomic free radicals is an important class of elementary reactions in high-temperature pyrolysis and combustion processes.<sup>1–3</sup> In any quantitative combustion modeling study, the proper inclusion of the kinetics of these reactions, including the pressure and temperature dependencies of their unimolecular rate constants, is essential.<sup>4,5</sup> The ultimate products formed by combustion processes, rates of burning, and temperature dependencies of flame properties are sensitive functions of the relative importances of the competing reactions of decomposition and other elementary reactions involving the same intermediates (e.g., reactions with atoms,  $O_2$ , and other free radicals).

Most of the current knowledge of the rate constants of these unimolecular reactions is derived from kinetic data on the reverse addition reactions combined with thermodynamic properties of the reactants and products.<sup>6</sup> In general, the kinetic data on the reverse reactions has 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 high-temperature chemical processes.

The method employed in the current study has been successfully used before in direct studies of the unimolecular decomposition of polyatomic hydrocarbon radicals. The experimental procedure makes it possible to isolate and quantitatively study the kinetics of the unimolecular decomposition of free radicals at elevated temperatures (up to  $\approx 1100$  K in selected cases) and at low pressures (1–10 Torr) where falloff from the high-

pressure limit can be significant.<sup>7,8</sup> 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  $\langle \Delta E \rangle_{down}$ , the average internal energy lost in deactivating collisions, for the conditions of the experiments but also an indication of the temperature dependence of this parameter.<sup>9,10</sup> Such temperature dependencies are required to extrapolate weakcollision effects observed under the relatively mild experimental conditions used in laboratory studies to the harsher conditions of combustion processes. To date the unimolecular decomposition of the following radicals has been studied using the above experimental method: HCO,<sup>7</sup> *n*-C<sub>5</sub>H<sub>11</sub>,<sup>8</sup> C<sub>2</sub>H<sub>5</sub>,<sup>9</sup> *i*-C<sub>3</sub>H<sub>7</sub>,<sup>10</sup> *n*-C<sub>3</sub>H<sub>7</sub>,<sup>11</sup> CH<sub>3</sub>CO,<sup>12</sup> CH<sub>3</sub>CHCl,<sup>13</sup> *t*-C<sub>4</sub>H<sub>9</sub>,<sup>14</sup> and *s*-C<sub>4</sub>H<sub>9</sub>.<sup>15</sup>

The current study addresses the reactions of unimolecular decomposition of the two remaining isomers of the butyl radical:  $n-C_4H_9$  and *iso*-C\_4H\_9. Rate constants for the reaction

$$n - C_4 H_9 \rightleftharpoons C_2 H_5 + C_2 H_4 \qquad (1, -1)$$

were measured at four densities of He ([He] =  $(3-18) \times 10^{16}$  molecules cm<sup>-3</sup>) and at two densities of N<sub>2</sub> ([N<sub>2</sub>] =  $(6-12) \times 10^{16}$  molecules cm<sup>-3</sup>) in the temperature range 560–620 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 the reaction (1,-1) was analyzed based on the data available in the literature as well as on modeling of our experimental results on reaction 1. A transition state model provided 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.

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The unimolecular decomposition of the *iso*-C<sub>4</sub>H<sub>9</sub> radical

$$iso-C_4H_9 \rightleftharpoons CH_3 + C_3H_6$$
 (2,-2)

could not be isolated for direct experimental study due to a contribution of other butyl radical isomers to the signal (see section II). Analysis of the data on the kinetics of nonterminal addition of methyl radicals to propylene (reaction -2) and the thermochemistry of reaction (2,-2) available in the literature, together with our ab initio study, resulted in a recommendation for the rate constants of this reaction.

The unimolecular decomposition of the *n*-C<sub>4</sub>H<sub>9</sub> and *iso*-C<sub>4</sub>H<sub>9</sub> radicals has not been isolated for direct study prior to this investigation. However, the rate constant of dissociation relative to that of recombination has been determined by both Kerr and Trotman-Dickenson<sup>16</sup> and Morganroth and Calvert<sup>17</sup> for *n*-C<sub>4</sub>H<sub>9</sub> radical and by Slater et al.<sup>18</sup> and Metcalfe and Trotman-Dickenson<sup>19</sup> for *iso*-C<sub>4</sub>H<sub>9</sub> radical. The reverse reactions (-1 and -2) have been studied by several groups.<sup>20–25</sup> Each of these investigations of both reactions 1 and -1 involved the study of complex reaction systems and will be discussed in detail in Section IV.

Recommendations for the temperature dependence of the rate constants of decomposition reactions have been provided by Warnatz<sup>1</sup> (reactions 1 and 2) and Tsang<sup>26</sup> (reaction 2) and of reaction -1 by Kerr and Parsonage<sup>27</sup> (based on the results of Kerr and Trotman-Dickenson<sup>22</sup> and Watkins and O'Dean<sup>23</sup>).

We have reanalyzed these relative studies of both the direct and reverse reactions (1,-1) and (2,-2) using new data available on the kinetics of the corresponding reference reactions and appropriate falloff corrections. This analysis together with the modeling of our experimental data resulted in recommendations for the high-pressure limit rate constants of these reactions as well as in information on weak collision effects in reaction (1,-1).

#### **II.** Experimental Study

Details of the experimental apparatus<sup>28</sup> and procedures<sup>8</sup> used have been described before and so are only briefly reviewed here. The *n*-butyl radicals were produced homogeneously at elevated temperatures in a heatable quartz tubular reactor by pulsed laser photolysis and their unimolecular decay subsequently monitored in time-resolved experiments using photoionization mass spectrometry. Pulsed unfocused 248-nm radiation ( $\approx$ 5 Hz) from a Lambda Physik EMG 201MSC excimer laser was directed along the axis of a heatable quartz reactor (1.05-cm i.d.) coated with boron oxide. Gas flowing through the tube at  $\approx$ 4 m s<sup>-1</sup> contained the radical precursor (<0.2%) and the inert carrier gas (He or N<sub>2</sub>) in large excess (>99.8%). The flowing gas was completely replaced between laser pulses.

The *n*-butyl radicals were produced by the pulsed, 248-nm laser photolysis of 1-bromobutane:

$$CH_3CH_2CH_2CH_2Br \xrightarrow{248 \text{ nm}} n-C_4H_9 + \text{ other products}$$
 (3)

Initial conditions (precursor concentration and laser intensity) were selected to provide low radical concentrations ( $\leq 10^{11}$  molecules cm<sup>-3</sup>). Under these conditions reactions between radical products (including *n*-C<sub>4</sub>H<sub>9</sub> + *n*-C<sub>4</sub>H<sub>9</sub>) had negligible rates compared to that of the unimolecular decomposition of the *n*-C<sub>4</sub>H<sub>9</sub> 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. *n*-Butyl radicals were ionized using the light from a chlorine resonance lamp (8.8-8.9 eV) with a CaF<sub>2</sub> 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 1000-30000 repetitions of the experiment were accumulated before the data were analyzed.

The gases used were obtained from Aldrich (1-bromobutane, 99%) and Matheson (He, >99.995%;  $N_2$ , >99.998%). 1-Bromobutane was purified by vacuum distillation prior to use. Helium and nitrogen were used as provided.

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

Unimolecular decay of n-C<sub>4</sub>H<sub>9</sub> was observed only above 500 K. Below this temperature a slow decay of n-C<sub>4</sub>H<sub>9</sub> is observed due to a first-order heterogeneous wall-loss process:

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

Above 500 K the decay constant increased rapidly with rising temperature due to the increasing importance of the thermal decomposition of the *n*-butyl radical, reaction 1. The *n*-C<sub>4</sub>H<sub>9</sub> decay constants were analyzed assuming that the *n*-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 500 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 500 K. While  $k_4$  was directly determined below 500 K (15–38 s<sup>-1</sup>, 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 500 K needed to determine  $k_1$  from the measurements of k' were obtained by an extrapolation assuming that k<sub>4</sub> retains its temperature independence beyond 500 K up to the highest temperature of this study, 620 K. To minimize possible errors in the determination of  $k_1$  caused by this assumed temperature independence of  $k_4$  above 500 K, experiments to obtain  $k_1$  were conducted at temperatures sufficiently high to ensure 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  $400 \text{ s}^{-1}$  could not be measured accurately.

A potentially complicating factor in these experiments is the production of other butyl radical isomers during the photolysis process. We studied the relative sensitivity of our experimental ion detection system for the four isomers of butyl radical using bromine and chlorine ionization lamps. A chlorine lamp with CaF2 window (used in the current study) provides ionizing radiation with photon energy 8.6-8.9 eV.<sup>29</sup> The most intense lines in the spectrum of a bromine ionization lamp with a sapphire window lie in the region 7.59-7.87 eV,<sup>29</sup> 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<sub>4</sub>H<sub>9</sub> (IP = 6.70 eV) and s-C<sub>4</sub>H<sub>9</sub> (IP = 7.25 eV).<sup>30</sup> The methods to generate the *tert*butyl and sec-butyl radicals were described earlier.14,15 iso-C<sub>4</sub>H<sub>9</sub> radicals were generated using the 248-nm photolysis of 1-bromo-2-methylpropane. The detection sensitivities obtained with the bromine and chlorine ionization lamps differed only by a factor of 2 for both *t*-C<sub>4</sub>H<sub>9</sub> and *s*-C<sub>4</sub>H<sub>9</sub> isomers (with better sensitivity obtained using the chlorine lamp). Although both *n*-C<sub>4</sub>H<sub>9</sub> and *iso*-C<sub>4</sub>H<sub>9</sub> 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 chlorine lamp was used. The absence of a strong ion signal at the mass of C<sub>4</sub>H<sub>9</sub> if a bromine ionizing lamp is used during the 248-nm photolysis of 1-bromobutane indicates the absence of significant concentrations of *t*-C<sub>4</sub>H<sub>9</sub> or *s*-C<sub>4</sub>H<sub>9</sub>.

Ethyl radical ( $C_2H_5$ ) was detected as a primary product of the unimolecular decomposition of the *n*-C<sub>4</sub>H<sub>9</sub> radical with the rise time of  $C_2H_5^+$  matching that of the decay of the *n*-butyl ion signal. No formation of  $C_3H_6$  (which is a primary product of the unimolecular decomposition of the *s*-C<sub>4</sub>H<sub>9</sub> isomer<sup>15</sup> and is expected to be the primary product of the thermal decomposition of *iso*-C<sub>4</sub>H<sub>9</sub> as well) was observed in the current study.

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  $t-C_4H_9$  earlier using the same experimental technique at T = 712 - 779 K.<sup>14</sup> The decomposition of the s-C<sub>4</sub>H<sub>9</sub> radical was studied<sup>15</sup> at T = 600-680 K, and the *iso*-C<sub>4</sub>H<sub>9</sub> isomer decomposes within an approximate temperature range 580-650 K. The current study of the thermal decomposition of the  $n-C_4H_9$  radical was limited to the 560-620 K temperature range. The absence of any significant ion signal if the bromine ionization lamp is used, together with the different temperature ranges in which the four butyl radical isomers decompose, and the absence of propene among the products of the radical decomposition permits us to eliminate the potential contribution of other butyl radical isomers to the  $n-C_4H_9$  signal under the conditions of our experimental study.

It was, however, not possible to eliminate such contributions to the signal of the *iso*-butyl radical. At 650 K, the temporal profile of the *iso*-C<sub>4</sub>H<sub>9</sub> ion signal exhibited a noticeable contribution of a slow-decaying (compared to a fast decay due to the decomposition) component. The relative contribution of this component significantly increased if a bromine ionization lamp was used. This indicates the possibility of the formation of some amount of *tert*-butyl radicals (which decompose at higher temperatures) in the photolysis of 1-bromo-2-methylpropane. Hence, the rate constants of the unimolecular decomposition of *iso*-C<sub>4</sub>H<sub>9</sub> could not be measured directly.

The results of all the experiments and the 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 1–3. 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.** Ab Initio Study of the *n*-Butyl and *iso*-Butyl Radicals and Decomposition Transition States

We studied the geometries and harmonic vibrational frequencies of n-C<sub>4</sub>H<sub>9</sub> and *iso*-C<sub>4</sub>H<sub>9</sub> radicals and decomposition transition states (n-C<sub>4</sub>H<sub>9</sub><sup>‡</sup> and *iso*-C<sub>4</sub>H<sub>9</sub><sup>‡</sup>) using the ab initio UHF method with the 6-31G\* basis. Energies were calculated at the MP2/6-31G\* method. Structures and vibrational frequencies of the most stable conformations of these species are listed in Tables 1S and 2S (supporting information). The GAUSSIAN 92 system of programs<sup>31</sup> was used in all ab initio calculations.

Internal rotations ( $-CH_2$  and  $-CH_3$  torsions and rotation about the C2-C3 bond) in n-C<sub>4</sub>H<sub>9</sub>, n-C<sub>4</sub>H<sub>9</sub><sup> $\ddagger$ </sup>, *iso*-C<sub>4</sub>H<sub>9</sub>, and *iso*-

TABLE 1: Conditions and Results of Experiments To Measure the Unimolecular Rate Constants  $(k_1)$  of the Thermal Decomposition of *n*-Butyl Radicals in He and N<sub>2</sub> as Bath Gases

$10^{-16}[M]$ (molecules cm <sup>-3</sup> )	<i>T</i> (K)	$\begin{array}{c} 10^{-13}\\ [n\text{-}C_4\text{H}_9\text{Br}]\\ (\text{molecules}\\ \text{cm}^{-3}) \end{array}$	$k_4$ (s <sup>-1</sup> )	$k_1 \ (s^{-1})$	master equation analysis $\langle \Delta E \rangle^{o}_{down}$ (cm <sup>-1</sup> )	master equation analysis $-\langle \Delta E \rangle_{all} (cm^{-1})$	
He as Bath Gas							
3	570	3.6	18.8	53.5	190	34	
3	580	3.6	18.8	83.6	214	41	
3	590	3.6	18.8	114	209	38	
3	600	3.6	26.0	144	193	31	
3	610	3.6	26.0	197	200	32	
3	620	3.6	26.0	256	194	30	
6	570	6.6	24.8	72.6	187	32	
6	570	6.6	21.0	78.9	210	40	
6	570	2.3	18.3	72.8	187	33	
6	580	6.6	24.8	112	208	38	
6	580	2.3	18.3	101	183	30	
6	590	11.0	32.2	144	188	31	
6	590	2.3	18.3	138	178	28	
6	600	11.0	32.2	180	168	25	
6	600	11.0	24.3	189	178	27	
6	610	11.0	32.2	253	176	25	
6	620	6.1	24.7	308	160	21	
12	560	8.1	19.6	60.2	165	27	
12	560	8.1	15.4	67.4	196	37	
12	570	8.1	19.6	93.3	181	30	
12	570	2.3	17.8	93.3	181	30	
12	580	8.1	19.6	132	177	28	
12	580	8.1	15.4	140	194	33	
12	590	8.1	19.6	179	169	26	
12	590	2.3	17.8	169	156	22	
12	600	5.4	35.6	234	156	22	
12	600	5.4	37.7	232	155	21	
12	610	5.4	35.6	340	170	24	
18	560	5.8	16.6	80.0	213	42	
18	570	5.8	16.6	114	201	37	
18	580	5.8	16.6	156	181	29	
18	590	5.8	16.6	220	180	28	
18	600	5.8	24.2	281	159	22	
		N.	as Ba	th Gas			
6	580	10.8	23.6	123	283	67	
6	580	10.8	31.0	112	265	54	
6	590	10.8	31.9	127	101	32	
6	600	10.8	31.9	175	193	31	
6	610	10.8	31.9	236	192	30	
12	570	10.8	32.3	96.6	225	45	
12	580	11.0	37.4	136	218	42	
12	590	11.0	37.4	166	180	28	
12	600	11.0	37.4	249	200	33	

 $C_4H_9^{\dagger}$  were studied by the MP2/6-31G\*//UHF/6-31G\* method. Geometrical structures corresponding to minima and maxima of the rotational potential energy surfaces were obtained with the full optimization at the UHF/6-31G\* level and energy was calculated at the MP2/6-31G\* level. The rotational energy barriers of the -CH<sub>3</sub> torsion and rotation about the C2-C3 bond are listed in Table 3S. The torsional motion of the -CH<sub>2</sub> group of the *n*-butyl radical was found to have a very small rotational barrier (6-fold barrier with the highest maximum only 0.8 kJ mol<sup>-1</sup> above the lowest minimum, correction for the zero-point vibrational energy included). Hence, it was treated as free rotation. The -CH<sub>2</sub> group torsional motion in the *iso*-C<sub>4</sub>H<sub>9</sub> radical also has a very small barrier (1.2 kJ mol<sup>-1</sup>) and, therefore, was also treated as free.

The optimized structure of the n-C<sub>4</sub>H<sub>9</sub> coincides with that determined by Pacansky et al.<sup>32</sup> using the same method. The conclusion about the low barriers for the rotation of the  $-CH_2$  group and the shape of the potential of the rotation about the C2–C3 bond are in an excellent agreement with analogous results of Pacansky et al. obtained for the case of *n*-hexyl radical.



**Figure 1.** Plot of *n*-C<sub>4</sub>H<sub>9</sub> unimolecular rate constants ( $k_1$  vs 1000/*T*) for different He densities (atom cm<sup>-3</sup>). Lines represent the results of master equation simulation using  $\langle \Delta E \rangle_{all} = -28 \text{ cm}^{-1}$ . Open circles, [He] = 3 × 10<sup>16</sup> atoms cm<sup>-3</sup>; closed circles, [He] = 6 × 10<sup>16</sup> atoms cm<sup>-3</sup>; open squares, [He] = 12 × 10<sup>16</sup> atoms cm<sup>-3</sup>; closed squares, [He] = 18 × 10<sup>16</sup> atoms cm<sup>-3</sup>.



**Figure 2.** Plot of n-C<sub>4</sub>H<sub>9</sub> unimolecular rate constants ( $k_1$  vs 1000/T) for different densities of N<sub>2</sub> (molecule cm<sup>-3</sup>). Lines represent the results of master equation simulation using  $\langle \Delta E \rangle_{all} = -40$  cm<sup>-1</sup>. Closed circles, [M] = 6 × 10<sup>16</sup> molecules cm<sup>-3</sup>; open squares, [M] = 12 × 10<sup>16</sup> molecules cm<sup>-3</sup>.

The models of the *n*-C<sub>4</sub>H<sub>9</sub> and *iso*-C<sub>4</sub>H<sub>9</sub> radicals used in the data analysis (next section) were built on the basis of the current ab initio study. The moments of inertia for the overall rotations and reduced moments of inertia for the internal rotations in radicals and decomposition transition states were calculated using the data of Table 1S. The calculated vibrational frequencies (scaled by a factor of 0.89) of the lowest-energy conformations of *n*-butyl and *iso*-butyl radicals were used in these models. The potential energy surface of the C2-C3 torsional motion in the  $n-C_4H_9$  radical has a complex form with three minima (conformations anti n-C<sub>4</sub>H<sub>9</sub> and gauche n-C<sub>4</sub>H<sub>9</sub> in Table 3S), two of them being identical (gauche  $n-C_4H_9$ ). In our model of the *n*-butyl radical, we assume a triple sinusoidal well with the barrier height of 18.6 kJ mol<sup>-1</sup>—the average of the barriers between the anti and gauche conformations and between the two gauche conformations.

One test of the appropriateness of the selected parameters of the *n*-butyl and *iso*-butyl radicals is to compare the calculated entropy with the values obtained from experiment. The roomtemperature entropies for the two butyl radical isomers were



**Figure 3.** Falloff curves,  $k_1$  vs [He] for seven temperatures used in the experiments (560–620 K). Lines represent the results of master equation simulation using  $\langle \Delta E \rangle_{all} = -28 \text{ cm}^{-1}$ .

calculated assuming separability of vibrational and rotational (including internal) degrees of freedom and using the values of Pitzer and Gwinn<sup>33</sup> for thermodynamic functions of the hindered internal rotors. The calculated values of  $S^{\circ}_{298}$  (332 and 320 J mol<sup>-1</sup> K<sup>-1</sup> for *n*-butyl and *iso*-butyl, respectively) coincides within error limits with the value obtained in the recent experimental study of Seetula and Slagle<sup>34</sup> (328 ± 5 and 316 ± 5 J mol<sup>-1</sup> K<sup>-1</sup>).

The results of the ab initio study of the decomposition transition states, n-C<sub>4</sub>H<sub>9</sub><sup>‡</sup> and *iso*-C<sub>4</sub>H<sub>9</sub><sup>‡</sup>, were also used in creating the models of reactions (1,-1) and (2,-2). Although the calculated reaction energy threshold values are not believed to be sufficiently accurate and are not used here, the geometrical configurations of the above transition states (Table 1S) and the barriers for internal rotations (Table 3S) were used in the models. The calculated sets of vibrational frequencies of the transition states were used as a basis for the models, with several lowest frequencies adjusted to fit the known temperature dependencies of the rate constants (section IV).

#### IV. Data Analysis

Transition-state theory formalism was used to model the highpressure limit rate constants of reactions (1,-1) and (2,-2). 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  $(k_1^{\infty}, k_{-1}^{\infty}, k_2^{\infty}, k_{-2}^{\infty})$  is first reviewed. Then, transitionstate models are created which reproduce the high-pressure limit rate constants of the reverse (association) reactions  $k_{-1}^{\infty}(T)$  and  $k_{-2}^{\infty}(T)$ . The density of states and sum of states functions of the *n*-butyl and *iso*-butyl radicals and the transition states, 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.<sup>14</sup> The transition-state models provide the values of the microcanonical rate constants, k(E), needed in the master equation modeling. The energy barrier height for the *n*-butyl 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. The selected model of reaction (1,-1) is used to obtain quantitative information on the weak



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**Figure 4.** Plot of experimental and calculated values of  $k_1^{\infty}$  vs 1000/*T*. Open circles, Morganroth and Calvert;<sup>17</sup> closed circles, Kerr and Trotman-Dickenson.<sup>16</sup> Solid line is obtained from the TST calculations using the model described in text, section IV.2. Dashed line represents the  $k_1$  values obtained using this model with  $\langle \Delta E \rangle^{\circ}_{\text{down}} = 500 \text{ cm}^{-1}$ under the conditions of the experiments of Kerr and Trotman-Dickenson (see text).

collision effects. The transition state model of reaction -2, in combination with the known thermochemistry of reaction (2,-2), provides the temperature dependence of the high-pressure limit rate constant of reaction 2,  $k_{2}^{\infty}(T)$ .

1. Experimental High-Pressure Limit Rate Constants of **Reactions** (1,-1) and (2,-2). Present knowledge of the kinetics of reaction (1,-1) and (2,-2) 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 transition-state models of reactions (1,-1) and (2,-1)2).

Decomposition Reaction  $n-C_4H_9 \rightarrow C_2H_5 + C_2H_4$  (1). Gierczak et al.35 studied chemically activated s-C<sub>4</sub>H<sub>9</sub> from the photolysis of H<sub>2</sub>S/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 and *n*-butyl radicals. No details of the model are reported, and it is not clear to what extent the results ( $A = 10^{13.65} \text{ s}^{-1}$ , threshold energy =  $121.8 \text{ kJ mol}^{-1}$ ) are affected by the assumptions and details of the model. We therefore did not consider the results of Gierczak et al.<sup>35</sup> in creating our transition-state model.

Kerr and Trotman-Dickenson<sup>16</sup> and Morganroth and Calvert<sup>17</sup> determined the decomposition rate constant relative to that of the recombination reaction 5. Kerr and Trotman-Dickenson<sup>16</sup>

$$n - C_4 H_9 + n - C_4 H_9 \rightarrow C_8 H_{18} \tag{5}$$

used medium-pressure mercury arc photolysis of n-valeraldehyde as a  $n-C_4H_9$  source. The experiments were conducted at an average concentration of valeraldehyde of  $4 \times 10^{17}$  molecules cm<sup>-3</sup> and temperatures in the range 477-689 K using final product analysis. Morganroth and Calvert<sup>17</sup> used 366-nm photolysis of azobutane with mass spectrometric and chromatographic analysis of products at T = 432-520 K and an average azobutane concentration of  $1.5 \times 10^{17}$  molecules cm<sup>-3</sup>.

To obtain  $k_1^{\infty}$  values from these relative measurements, knowledge of the rate constant for the recombination of *n*-butyl

**Figure 5.** Plot of experimental and calculated values of  $k_2^{\infty}$  vs 1000/*T*. Squares, Slater et al.;<sup>18</sup> circles, Metcalfe and Trotman-Dickenson.<sup>19</sup> Open symbols, experimental values of  $k_2$ ; closed symbols, "experimental" values corrected for the falloff effects (see text). Solid line is obtained from the TST calculations using the model described in text, section IV.4. Dashed line, recommendation by Tsang.<sup>26</sup>

radicals,  $k_5$ , is required. No experimental data are available on this reaction. We assume here that  $k_5$  equals the rate constant of the recombination of n-propyl radicals. Taking the recommendation of Tsang<sup>36</sup> for the latter value, we obtain  $k_5 = 1.7$  $\times$  10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Using this expression and the results of Kerr and Trotman-Dickenson<sup>16</sup> and of Morganroth and Calvert,<sup>17</sup> values of  $k_1$  are obtained which can be fitted with simple Arrhenius expressions in the experimental temperature ranges of these authors. We obtain

$$k_1(\text{KTD}) = 7.73 \times 10^{10} \exp(-11349 \text{ K/T}) \text{ s}^{-1}$$
 (I)

from the results of Kerr and Trotman-Dickenson and

$$k_1(\text{MC}) = 2.58 \times 10^{13} \exp(-14481 \text{ K/T}) \text{ s}^{-1}$$
 (II)

from the results of Morganroth and Calvert (Figure 4).

Decomposition reaction iso- $C_4H_9 \rightarrow CH_3 + C_3H_6$  (2). Metcalfe and Trotman-Dickenson<sup>19</sup> and Slater et al.<sup>18</sup> determined the iso-C<sub>4</sub>H<sub>9</sub> decomposition rate constants relative to that of the recombination reaction 6:

$$iso-C_4H_9 + iso-C_4H_9 \rightarrow C_8H_{18}$$
 (6)

Metcalfe and Trotman-Dickenson used the photoinitiated chain decomposition of isovaleraldehyde with product analysis by gas chromatography. Their experiments were conducted at temperatures in the range 552-691 K and concentrations of isovaleraldehyde (the main component of the bath gas) (4.0-7.2)  $\times$  10<sup>17</sup> molecules cm<sup>-3</sup>. Slater et al. used the 366-nm photolysis of 1,1'-azoisobutane with gas chromatographic analysis of products at T = 543-598 K and an average pressure of 1,1'-azoisobutane of 5.4 Torr.

The rate constants of reaction 6 have not been determined experimentally. Following the recommendation by Tsang,<sup>26</sup> we use the value of the rate constant of the recombination of  $n-C_3H_7$ radicals<sup>36</sup> for reaction 6. The resultant values of  $k_2$  obtained from the relative measurements of Metcalfe and Trotman-Dickenson<sup>19</sup> and Slater et al.<sup>18</sup> are shown in Figure 5. As can

## TABLE 2: Models of the Molecules and Transition States Used in the Data Analysis

Energy Barriers  $E_1$  (reaction 1) = 115.8 kJ mol<sup>-1</sup>;  $E_2$  (reaction 2) = 126.6 kJ mol<sup>-1</sup>  $E_{-1}$  (reaction -1) = 28.0 kJ mol<sup>-1</sup>;  $E_{-2}$  (reaction -2) = 37.2 kJ mol<sup>-1</sup> N-C<sub>4</sub>H<sub>9</sub>: Vibrational Frequencies (cm<sup>-1</sup>) n-C<sub>4</sub>H<sub>9</sub>: 250, 398, 433, 702, 788, 836, 928, 977, 1020, 1059, 1135, 1223, 1284, 1290, 1373, 1394, 1425, 1450, 1458, 1463, 1472, 2789, 2841, 2846, 2849, 2871,

- $\begin{array}{c} \begin{array}{c} 2901,\,2903,\,2944,\,3030\\ n\text{-}C_4\text{H}_9^{\ddagger} \end{array} \\ \begin{array}{c} \begin{array}{c} 2901,\,2903,\,2944,\,3030\\ 374,\,400,\,500,\,700,\,800,\,900,\,900,\,900,\,900,\,950,\\ 1000,\,1047,\,1137,\,1187,\,1193,\,1384,\,1420,\,1438,\\ 1455,\,1458,\,1589,\,2825,\,2876,\,2901,\,2928,\,2951,\\ 2961,\,3000,\,3020,\,3042 \end{array} \right. \end{array}$

- $\begin{array}{ccc} C_2H_5 & & 3112, 3033, 2987, 2920, 2842, 1511, 1496, 1440, \\ & & 1366, 1175, 1138, 1000, 821, 540 \end{array}$

#### Rotational Constants (cm<sup>-1</sup>),Symmetry Numbers, and Rotational Barriers (kJ mol<sup>-1</sup>)

	Overall Rotations
<i>n</i> -C <sub>4</sub> H <sub>9</sub> :	$A = 0.6566; \sigma = 1$ (active)
	$(BC)^{1/2} = 0.1009; \sigma = 1 \text{ (inactive)}$
$n-C_4H_9^{\mp}$ :	$A = 0.847; \sigma = 1$ (active)
	$(BC)^{1/2} = 0.122; \sigma = 1 \text{ (inactive)}$
iso-C <sub>4</sub> H <sub>9</sub> :	$A = 0.2805; \sigma = 1$ (active)
	$(BC)^{1/2} = 0.2023; \sigma = 1 \text{ (inactive)}$
iso-C <sub>4</sub> H <sub>9</sub> *:	$A = 0.2626; \sigma = 1$ (active)
	$(BC)^{1/2} = 0.1600; \sigma = 1$ (inactive)
$C_2H_5$ :	$(ABC)^{1/3} = 1.227; \sigma = 1$
	Internal Rotations
$n-C_4H_9$ :	$a_1(CH_3-CH_2CH_2CH_2) = 6.256; \sigma = 3; V_0 = 14.25$
	$a_2(CH_3CH_2-CH_2CH_2) = 1.644; \sigma = 1; V_0 = 18.61$
	$a_3(CH_3CH_2CH_2-CH_2) = 10.47; \sigma = 2; V_0 = 0$
$n - C_4 H_9^{\ddagger}$ :	$a_1(CH_3-CH_2CH_2CH_2) = 5.919; \sigma = 3; V_0 = 7.82$
	$a_2(CH_3CH_2\cdots CH_2CH_2) = 1.606; \sigma = 1; V_0 = 2.32$
iso-C4H9:	$a_{1,2}(CH_3-CH(CH_3)CH_2) = 5.703; \sigma = 3; V_0 = 16.84$
	$a_3(CH_3CH(CH_3)-CH_2) = 9.979; \sigma = 2; V_0 = 0$
iso-C <sub>4</sub> H <sub>9</sub> <sup>‡</sup> :	$a_1(CH_3CH(-CH_3)CH_2) = 5.643; \sigma = 3; V_0 = 7.39$
	$a_2(CH_3 \cdots CH(CH_3)CH_2) = 5.315; \sigma = 3; V_0 = 3.86$
C2He:	$a(CH_2 - CH_2) = 15.16; \sigma = 6; V_0 = 0$

Lennard-Jones Parameters<sup>a</sup>

gas	$\epsilon/k$ (K)	$\sigma$ (Å)
Не	10.22	2.551
$N_2$	71.4	3.798
$n-C_4H_9^b$	531.4	4.687
iso-C <sub>4</sub> H <sub>9</sub> <sup>c</sup>	330.1	5.278

 $^a$  From ref 44.  $^b$  Taken to be the same as for  $n\text{-}C_4H_{10}$ .  $^c$  Taken to be the same as for  $iso\text{-}C_4H_{10}$ .

be seen from Figure 5, the results of these two studies are in significant disagreement. The rate constants of Slater et al. are more than an order of magnitude lower than those of Metcalfe and Trotman-Dickenson. It has been noted by  $Tsang^{26}$  that the methodology used by Slater et al. results in an unacceptably low value for the rate of the isobutyl radical reaction with O<sub>2</sub>. It will be shown later (Section IV.5) that the results of both these studies are in the falloff region.

Association (Reverse) Reaction  $C_2H_5 + C_2H_4 \rightarrow n-C_4H_9$  (-1). The addition of ethyl radical to the double bond of ethylene has been studied by four groups.<sup>20–23</sup> In all cases ratios of  $k_{-1}$ to the square root of the  $C_2H_5$  recombination rate constant were determined by product analysis in complex reaction systems. These results were analyzed by Kerr and Parsonage<sup>27</sup> who, based on the results of Kerr and Trotman-Dickenson<sup>22</sup> and of Watkins and O'Dean,<sup>23</sup> recommended  $k_{-1} = 2.63 \times 10^{-13} \exp(-3674$ K/T) cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This expression was obtained by assuming the rate constant of C<sub>2</sub>H<sub>5</sub> recombination,  $k_7$ , to be equal to  $4.2 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Using the value recommended by Baulch et al.,<sup>37</sup>  $k_7 = 1.9 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, we obtained the expression at T = 348-482 K (combined temperature interval of experimental measurements of Kerr and Trotman-Dickenson and of Watkins and O'Dean)

$$k_{-1} = 1.78 \times 10^{-13} \exp(-3674 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
(III)

which was used in further analysis.

Association Reaction  $CH_3 + C_3H_6 \rightarrow iso-C_4H_9$  (-2). The recommendation for the rate constants of the nonterminal addition of methyl radical to propylene (reaction -2) is based on our analysis of the reaction -2', the terminal addition of CH<sub>3</sub> to C<sub>3</sub>H<sub>6</sub>:<sup>15</sup>

$$CH_3 + C_3H_6 \rightarrow sec - C_4H_9$$
 (-2')

The relative importance of terminal (reaction -2') and nonterminal (reaction -2) addition of methyl radical to propylene was analyzed by Baldwin et al.<sup>25</sup> Their recommendation  $(k_{-2'}/(k_{-2} + k_{-2'})$  equal to 0.735 at 753 K and 0.9 at 403 K) was based on their experimental study of the addition of CH<sub>3</sub> to propylene relative to the reaction of CH<sub>3</sub> with H<sub>2</sub> and on the results of the relative rates study of Cvetanovic and Irwin.<sup>24</sup> Following this recommendation and using our Arrhenius dependence of  $k_{-2'}$  ( $k_{-2'} = 1.81 \times 10^{-12} \exp(-4239 \text{ K/T}) \text{ cm}^3$ molecule<sup>-1</sup> s<sup>-1</sup>),<sup>15</sup> we obtain

$$k_{-2} = 2.53 \times 10^{-12} \exp(-5260 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
(IV)

at T = 403 - 753 K.

**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.

Calculation of  $k_1^{\infty}$  and  $k_{-1}^{\infty}$  requires knowledge of the structure and vibrational frequencies of the involved molecules. The geometric structure and vibrational frequencies of the ethylene molecule are known.<sup>38,39</sup> The moments of inertia of C<sub>2</sub>H<sub>5</sub> were taken from an ab initio study of Chen.<sup>40</sup> Experimentally observed<sup>41</sup> vibrational frequencies were used together with the UMP2/6-311G\*\* values of Pacansky et al.<sup>42</sup> for modes for which no experimental determinations were available. The internal rotation about the C–C bond was treated as free.<sup>43</sup> Table 2 lists the molecular parameters of C<sub>2</sub>H<sub>5</sub> used in the current study.

The model of the *n*-C<sub>4</sub>H<sub>9</sub> radical was taken from the results of the ab initio study (section III). All hindered rotations were treated classically in order to maintain compatibility with classical expressions for the density-of-states and sum-of-states functions of a hindered internal rotor<sup>14</sup> which are required for later calculation of energy-specific rate constants, k(E). The errors in the values of rate constants due to this classical approach are less than 4% for  $k_{-1}^{\infty}$  and less than 6% for  $k_{1}^{\infty}$  at temperatures higher than 298 K, as determined by comparing classical partition functions with exact tabulated values.<sup>33</sup>

 $k_{-1}^{\infty}$  is given by<sup>45</sup>

$$k_{-1}^{\infty} = \frac{k_{\rm B}T}{h} \frac{Q^{\dagger}}{Q_{\rm C_2H_4}Q_{\rm C_2H_5}} \exp\left(-\frac{E_{-1}}{k_{\rm B}T}\right)$$

where  $Q^{\ddagger}$ ,  $Q_{C_2H_5}$ , and  $Q_{C_2H_4}$  are partition functions of the transition state, ethyl radical and ethylene molecule respectively, and  $E_{-1}$  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 and the barriers for hindered internal rotations were taken from the results of the ab initio study (section III, Tables 1S and 3S). The lowest vibrational frequencies of the transition state and the addition energy barrier height for the association reaction  $E_{-1}$  were varied to fit Arrhenius expression III at temperatures in the range 348-482 K. Frequencies and other parameters of the transition state obtained through this fitting procedure are listed in Table 2. Since hindered internal rotations in  $n-C_4H_9$ and  $C_2H_5$  and in 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 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:

$$k_{-1}^{\infty} = 6.59 \times 10^{-21} T^{2.44} \exp(-2697 \text{ K/T})$$
  
cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (V)

The barrier to dissociation of the *n*-C<sub>4</sub>H<sub>9</sub> radical was obtained from the master equation/RRKM fitting of our experimental data (section IV.3). The *n*-butyl radical has no optical isomers, no overall rotational symmetry, and three internal rotors (-CH<sub>3</sub>, -CH<sub>2</sub>, and C2-C3) with symmetry factors of 3, 2, and 1--total symmetry factor 6. The transition state has two internal rotors (-CH<sub>3</sub> and C2-C3) with symmetry factors of 3 and 1. Since no optical isomerism is involved, we obtain<sup>45</sup> the reaction path degeneracy of 2 for the decomposition reaction.

3. Master Equation Calculations of  $k_1(T,[M])$  and Determinations of the Energy Barrier for Decomposition of n-C<sub>4</sub>H<sub>9</sub>,  $\langle \Delta E \rangle^{\circ}_{down}$ , and  $\langle \Delta E \rangle_{all}$ . The measured rate constants of reaction 1 ( $k_1(T,[M])$ ) were reproduced using master equation simulations. The "exponential down" model<sup>45,46</sup> of collisional energy transfer was adopted to characterize the probability of deactivation of the *n*-C<sub>4</sub>H<sub>9</sub> 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:

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

 $\langle \Delta E \rangle_{\text{down}}$  is the average energy lost in deactivating collisions, and *A* is a normalization constant.

It has been shown that accounting for the dependence of  $\langle \Delta E \rangle_{\text{down}}$  on E results in a change of shape of the falloff curve.<sup>47</sup> We express this dependence in the form  $\langle \Delta E \rangle_{\text{down}}(E) =$  $\langle \Delta E \rangle^{\circ}_{\text{down}} (E/E_1)^{0.5}$  where  $E_1$  is the barrier to dissociation,  $\langle \Delta E \rangle^{\circ}_{\text{down}}$  is the value of  $\langle \Delta E \rangle_{\text{down}}$  at  $E = E_1$ . This square-root functional form of the dependence of  $\langle \Delta E \rangle_{\text{down}}$  on energy results in an approximate dependence of  $\langle \Delta E \rangle_{all} \propto E (\langle \Delta E \rangle_{all}$  is the average energy lost in both activating and deactivating collisions) which is appropriate for large molecules.<sup>48,49</sup> To estimate the importance of inclusion of the energy dependence of  $\langle \Delta E \rangle_{\rm down}$  in the modeling method, we compared the values of the rate constants of reaction 1 calculated with and without accounting for this energy dependence. If  $\langle \Delta E \rangle_{\text{down}}$  values are chosen in such a way that low-pressure-limit rate constants coincide in these two cases, the calculated rate constant difference is  $\approx 20\%$  at the conditions of our experiments.

The energy-dependent rate constants k(E) were calculated using the RRKM method.<sup>45,50</sup> The density of states and sum of states functions of the *n*-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.<sup>14</sup> The density of states function was calculated separately for each hindered internal rotor of the *n*-C<sub>4</sub>H<sub>9</sub> 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.<sup>51</sup> The sum of states function for the transition state was similarly calculated.

To account for the angular momentum conservation effects, a method introduced by Marcus<sup>52</sup> was used. In this method, rate constants obtained originally without accounting for adiabatic rotations are multiplied by a factor  $I^{\ddagger}/I$ , and the low-pressure limit rate constant is also multiplied by a factor

$$F_{\rm rot} = \varrho[E_1 + (1 - I^{\ddagger}/I)k_{\rm B}T]/\varrho[E_1]$$

where  $\rho(E)$  is the density of states function of the excited molecule at energy E,  $I^{\ddagger}$  and I are the moments of inertia of the adiabatic rotational degrees of freedom of the transition state and n-C<sub>4</sub>H<sub>9</sub> molecule. Thus, falloff curves are "shifted" along the ln(P) axis by ln( $F_{\text{rot}}$ ). It has been shown<sup>50,53</sup> that this simple treatment is accurate at  $I^{\ddagger}/I \leq 3$ .  $I^{\ddagger}/I$  equals 1.22 for n-C<sub>4</sub>H<sub>9</sub> and 1.26 for *iso*-C<sub>4</sub>H<sub>9</sub>.  $F_{\text{rot}}$  for both molecules equals approximately 0.9 at 600 K.

The method of Gaynor et al.<sup>45,54</sup> for solving the master equation was employed. The energy bin size used in the fitting procedures was  $30 \text{ cm}^{-1}$ . 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 of states and sum of states functions, as well as from numerical integration, are not more than 7% of the exact values at the temperatures of the experiments.

The optimum value of the energy barrier for the decomposition,  $E_1$ , was obtained using a grid search with a step size of 1 kJ mol<sup>-1</sup>. With each fixed value of  $E_1$  a weighted sum of squares of deviations between calculated and experimental rate constants was minimized using collisional energy-transfer parameters ( $\langle \Delta E \rangle^{\circ}_{down}$  or  $\langle \Delta E \rangle_{all}$ ) as adjustable. Each data point was assigned a weight of 1/k1. The optimized values of this weighted sum of squares of deviations were obtained as a function of  $E_1$  and fitted with a parabolic function in the vicinity of the minimum. This procedure was repeated for the data obtained with He as bath gas assuming three models of the temperature dependence of  $\langle \Delta E \rangle^{\circ}_{\text{down}}$ . First,  $\langle \Delta E \rangle^{\circ}_{\text{down}}$  was taken as independent of temperature,  $\langle \Delta E \rangle^{\circ}_{\text{down}} = \text{constant}$ . Second, it was assumed to be directly proportional to temperature,  $\langle \Delta E \rangle^{\circ}_{\text{down}} = \alpha T$ . The latter model is based on the earlier studies of the reaction

$$C_2 H_5 \rightleftharpoons H + C_2 H_4 \tag{7}$$

The analysis of this system<sup>9</sup> demonstrated a strong dependence of  $\langle \Delta E \rangle_{\text{down}}$  on temperature, increasing from 70–100 cm<sup>-1</sup> at 300 K to 280 cm<sup>-1</sup> at 1100 K. This dependence was best fit with the directly proportional dependence,  $\langle \Delta E \rangle_{\text{down}} = 0.255T$ cm<sup>-1</sup>. The analysis of the *i*-C<sub>3</sub>H<sub>7</sub>  $\rightarrow$  H + C<sub>3</sub>H<sub>6</sub> system<sup>10</sup> also supports a strong temperature dependence of  $\langle \Delta E \rangle_{\text{down}}$  for He as bath gas.

TABLE 3: Optimized Values of the Energy Barrier Height  $E_1$ ,  $\langle \Delta E \rangle_{\text{down}}^{\circ}$ , and  $\langle \Delta E \rangle_{\text{all}}^{\circ}$  of Reaction 1 from the Master Equation Modeling (Section IV.3)

model of $\langle \Delta E \rangle_{\text{down}}$ vs <i>T</i> dependence	$E_1/\mathrm{kJ}~\mathrm{mol}^{-1}$	$\langle \Delta E \rangle^{\circ}_{ m down}  { m or}  \langle \Delta E \rangle_{ m all} / cm^{-1}$
$ \langle \Delta E \rangle^{\circ}_{\text{down}} = \alpha T  \langle \Delta E \rangle^{\circ}_{\text{down}} = \text{constant}  \langle \Delta E \rangle_{\text{all}} = \text{constant} $	115.7 116.1 115.8 (accepted in model)	$ \begin{array}{l} \langle \Delta E \rangle^{\circ}_{\rm down} = 0.295 T/{\rm K} \\ \langle \Delta E \rangle^{\circ}_{\rm down} = 192 \\ \langle \Delta E \rangle_{\rm all} = -28 \end{array} $

In the third model of the temperature dependence of  $\langle \Delta E \rangle_{\text{down}}^{\circ}$ , it was assumed that  $\langle \Delta E \rangle_{\text{all}}$  is independent of temperature. This represents an intermediate case of the  $\langle \Delta E \rangle_{\text{down}}$  vs *T* dependence, one in which  $\langle \Delta E \rangle_{\text{down}}$  still increases with *T* but more slowly than in the case of the directly proportional model.

The resultant optimized values of  $E_1$  obtained with these three models of the temperature dependence of  $\langle \Delta E \rangle_{\text{down}}$  from the analysis of the experimental data are listed in Table 3. Reaction 1 is close to the high-pressure limit under the conditions of our experiments  $(k_1([M],T)/k_1^{\infty} = 0.15 - 0.50$  if the model with  $E_1$ = 115.8 kJ mol<sup>-1</sup> 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 E1 obtained with the three models of the temperature dependence of  $\langle \Delta E \rangle_{\text{down}}$ is only 0.4 kJ mol<sup>-1</sup>. We select for further use in our model of reaction (1,-1) (Table 2) the value of  $E_1 = 115.8 \text{ kJ mol}^{-1}$ obtained assuming  $\langle \Delta E \rangle_{all}$  independent of temperature (model 3-intermediate case between models 1 and 2). The uncertainty of  $E_1$  obtained from the fitting procedure is 0.6 kJ mol<sup>-1</sup>. We estimate the total uncertainty of  $E_1$  as twice the sum of the above value and the difference between individual values of the energy barrier for the decomposition of n-C<sub>4</sub>H<sub>9</sub> in Table 3. Hence, we obtain  $E_1 = 115.8 \pm 2.0 \text{ kJ mol}^{-1}$ .

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

$$k_1^{\infty} = 1.06 \times 10^{13} \exp(-14005 \text{ K/T}) \text{ s}^{-1}$$
 (VII)

which is plotted in Figure 4 together with the experimental determinations of ref. 16 and 17.

Individual values of  $\langle \Delta E \rangle^{\circ}_{down}$  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  $\langle \Delta E \rangle^{\circ}_{down}$  as an adjustable parameter. Such calculations were performed with the selected model of the reaction. The resultant values of  $\langle \Delta E \rangle^{\circ}_{down}$  and  $\langle \Delta E \rangle_{all}$  are listed in Table 1. The average value of  $\langle \Delta E \rangle_{all}$  for He is  $-30 \text{ cm}^{-1}$  consistent (as expected) with the value  $-28 \text{ cm}^{-1}$  obtained in the "global" fitting procedure. The average value for N<sub>2</sub> as bath gas is  $\langle \Delta E \rangle_{all}$  $= -40 \text{ cm}^{-1}$ . Due to the scatter of individual values no information on the temperature dependence of  $\langle \Delta E \rangle^{\circ}_{down}$  or  $\langle \Delta E \rangle_{all}$  can be extracted from these results.

The values of the rate constants  $k_1([M],T)$  calculated using the accepted model of the reaction (Tables 2 and 3) and values of  $\langle \Delta E \rangle_{all} = -28 \text{ cm}^{-1}$  for He and  $\langle \Delta E \rangle_{all} = -40 \text{ cm}^{-1}$  for N<sub>2</sub> are presented in Figures 1–3 together with the experimental data.

A check of the quality of the model and data analysis procedure is provided by an inspection of the pressure dependence of  $\langle \Delta E \rangle^{\circ}_{\text{down}}$  or  $\langle \Delta E \rangle_{\text{all}}$ . The fitted values of these energytransfer parameters should exhibit no dependence on pressure. If the values of  $\langle \Delta E \rangle^{\circ}_{\text{down}}$  and  $\langle \Delta E \rangle_{\text{all}}$  from Table 1 are plotted vs pressure, no dependence can be seen which indicates that the model describes all sections of falloff in helium and nitrogen equally well in the experimental pressure range.

The  $\langle \Delta E \rangle_{all} = \text{constant}$  form of the temperature dependence of collisional parameters for He, obtained as an intermediate case between two extremes ( $\langle \Delta E \rangle_{down} = \text{constant}$  and  $\langle \Delta E \rangle_{down} = \alpha T$ ), was advocated by several groups. This independence of  $\langle \Delta E \rangle_{all}$  on temperature is consistent with the results of experimental and trajectory studies of collisional energy transfer in large polyatomic molecules.<sup>55,56</sup> The recent results of Kiefer et al.<sup>57</sup> on the thermal decomposition of CF<sub>3</sub>Cl in Kr at temperatures of 1521–3059 K were best fit with the constant value of  $\langle \Delta E \rangle_{all} = 270 \text{ cm}^{-1}$ . Dashevskaya et al.<sup>58</sup> predict  $\langle \Delta E \rangle_{all} = \text{constant}$  dependence for He as a bath gas in the framework of the sequential direct encounter model.

4. Transition-State Model of Reaction (2,-2). The development of a transition-state model for reaction (2,-2) was based on expression IV for the temperature dependence of the rate constant of reaction (-2). The same approach was used as in developing the model of reaction (1,-1), except for the selection of the  $E_2$  value.

The geometric structure and vibrational frequencies of the methyl radical and propylene as well as the barrier for the internal rotation in the propylene molecule are known.<sup>59,60</sup> The models of *iso*-C<sub>4</sub>H<sub>9</sub> and *iso*-C<sub>4</sub>H<sub>9</sub><sup>‡</sup> were taken from the results of the ab initio study (section III). The lowest vibrational frequencies of the transition state and the addition energy barrier height for the association reaction  $E_{-2}$  were varied to fit Arrhenius expression IV at temperatures in the range 403–753 K. Frequencies and other parameters of the transition state obtained through this fitting procedure are listed in Table 2.

The barrier to dissociation of the *iso*-C<sub>4</sub>H<sub>9</sub> radical,  $E_2$ , was obtained from the known thermochemistry of the involved species. Using  $\Delta H_{\rm f}^{\circ}_{298}(iso$ -C<sub>4</sub>H<sub>9</sub>) = 72.7 ± 2.2 kJ mol<sup>-1</sup>,<sup>34</sup>  $\Delta H_{\rm f}^{\circ}_{298}(CH_3) = 146.0 \pm 1.0$  kJ mol<sup>-1</sup>,<sup>61,62</sup>  $\Delta H_{\rm f}^{\circ}_{298}(C_3H_6) = 20.0 \pm 0.8$  kJ mol<sup>-1</sup>,<sup>63</sup> we obtain E<sub>2</sub> = 126.6 kJ mol<sup>-1</sup>. The isobutyl radical has no optical isomers, no overall rotational symmetry, and three internal rotors (2 –CH<sub>3</sub> and –CH<sub>2</sub>) with symmetry factors of 3, 3, and 2—total symmetry factor 18. The transition state has two internal –CH<sub>3</sub> rotors with symmetry factors of 3 each. Taking into account the existence of two optical isomers in the transition state, we obtain<sup>45</sup> a reaction path degeneracy of 4 for the decomposition reaction.

The model of the transition state described above results in the following expressions for the high-pressure limit rate constants of reaction (2,-2) at T = 298-1500 K:

$$k_{-2}^{\infty} = 1.66 \times 10^{-20} T^{2.57} \exp(-3879 \text{ K/T})$$
  
 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (VIII)}$   
 $k_2^{\infty} = 2.14 \times 10^{12} T^{0.65} \exp(-15529 \text{ K/T}) \text{ s}^{-1} \text{ (IX)}$ 

5. Analysis of Prior Experimental Studies of Reactions (1,-1) and (2,-2). Both experimental determinations of  $k_{-1}$ , those of Kerr and Trotman-Dickenson<sup>22</sup> and Watkins and O'Dean,<sup>23</sup> were performed under the conditions of the high-pressure limit, as checked by calculating the values of  $k_1(T,[M])/k_1^{\infty}$  at the temperatures and pressures of these experiments. The values of  $\langle \Delta E \rangle_{\text{down}} = 500$  and 800 cm<sup>-1</sup> were assigned to C<sub>2</sub>H<sub>4</sub> and propionaldehyde which were the bath gases in refs 22 and 23, respectively.

As can be seen from the comparison of the experimental values of  $k_1^{\infty}$  and the calculated results (Figure 4), the results of Morganroth and Calvert<sup>17</sup> are well reproduced by expression VII. The results of Kerr and Trotman-Dickenson,<sup>16</sup> although being in approximate agreement with formula VII at T = 500-

600 K, are somewhat higher at lower temperatures and significantly lower at higher temperatures. The experimental study of reaction 1 by Morganroth and Calvert<sup>17</sup> was practically in the high-pressure limit  $(k_1/k_1^{\infty} = 1 \text{ if } \langle \Delta E \rangle_{\text{down}} = 800 \text{ cm}^{-1}$  is assigned to 1,1'-azo-*n*-butane, the bath gas used in ref 17). The data of Kerr and Trotman-Dickenson on  $k_1$  are not exactly in the high-pressure limit. Assigning  $\langle \Delta E \rangle_{\text{down}} = 800 \text{ cm}^{-1}$  to *n*-valeraldehyde (bath gas of ref 16) yields  $k_1/k_1^{\infty}(689 \text{ K}) = 0.7$ , and using  $\langle \Delta E \rangle_{\text{down}} = 500 \text{ cm}^{-1}$ , we obtain  $k_1/k_1^{\infty}(689 \text{ K}) = 0.6$ . The Lennard-Jones collisional parameters used were estimated from the boiling point and additive volume increments.<sup>44</sup> Falloff, however, can only partially account for the difference between the calculated values of  $k_1^{\infty}$  and experimental results of Kerr and Trotman-Dickenson (Figure 4).

Both experimental determinations of  $k_2$  (Slater et al.<sup>18</sup> and Metcalfe and Trotman-Dickenson<sup>19</sup>) were performed under the conditions of falloff. Using the above model of reaction (2,– 2) and assigning  $\langle \Delta E \rangle_{down} = 800 \text{ cm}^{-1}$  to 1,1'-azoisobutane and isovaleraldehyde (the bath gases used by these authors) we obtain the values of  $k_2/k_2^{\infty}$  equal to 0.39–0.54 for the conditions of Slater et al. and 0.48–0.79 for the conditions of Metcalfe and Trotman-Dickenson. The Lennard-Jones collisional parameters used were estimated from the boiling point and additive volume increments.<sup>44</sup> "Experimental" values of  $k_2^{\infty}$  can be determined by dividing the experimental  $k_2$  by the calculated  $k_2/k_2^{\infty}$  values. The values of  $k_2$  and  $k_2^{\infty}$  thus obtained from the results of refs 18 and 19 are shown in Figure 5 together with our calculated  $k_2^{\infty}$ .

It can be seen from Figure 5 that taking into account the falloff correction significantly improves the agreement between the "experimental" values of  $k_2^{\infty}$  obtained from the data of Metcalfe and Trotman-Dickenson and those predicted by our model of reaction 2. The calculated and "experimental" values coincide in the middle of the experimental temperature range, although the "experimental" results display a slightly lower activation energy than the calculated ones. The results of Slater et al. are in significant disagreement with both the results of Metcalfe and Trotman-Dickenson and with our calculated values. Even after correcting for the falloff effects, the values of  $k_2^{\infty}$  obtained from the results of ref 18 are more than an order of magnitude lower than those of ref 19 and our calculated  $k_2^{\infty}$ .

Tsang<sup>26</sup> recommended the  $k_2^{\infty}(T)$  dependence  $(k_2^{\infty} = 2 \times 10^{13} \text{exp}(-15075 \text{ K/}T) \text{ s}^{-1})$  as a compromise between the results of Metcalfe and Trotman-Dickenson and values calculated from thermochemistry assuming 10% nonterminal addition of CH<sub>3</sub> to C<sub>3</sub>H<sub>6</sub> and a preexponential factor of 2 × 10<sup>13</sup> s<sup>-1</sup>. Tsang's recommendation is lower than that given by formula IX (a factor of 3 at 600 K). The difference is mainly due to the differences in approach and in the temperature dependencies of  $k_{-2}^{\infty}(T)$  used.

6. Thermochemistry of the *n*-C<sub>4</sub>H<sub>9</sub> 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 *n*-butyl radical. The recommended value of  $E_1 = 115.8 \pm 2.0 \text{ kJ mol}^{-1}$  together with the fitted value of the barrier for the reverse reaction,  $E_{-1} = 28.0 \text{ kJ mol}^{-1}$ , gives the energy difference between reactants and products of reaction (1,-1):  $\Delta E_{1,-1} = 87.8 \text{ kJ mol}^{-1}$ . Using the models of *n*-C<sub>4</sub>H<sub>9</sub>, C<sub>2</sub>H<sub>5</sub>, and C<sub>2</sub>H<sub>4</sub> described above and taking into account the zeropoint energies of the torsional rotations (excluded from  $E_1$  and  $\Delta E_{-1}$ ), one can obtain for the enthalpy of reaction (1,-1)  $\Delta H^{\circ}_{298} = 89.4 \text{ kJ mol}^{-1}$ . With  $\Delta H_{1}^{\circ}_{298}(C_{2}H_{5}) = 121.0 \pm 1.5 \text{ kJ mol}^{-1}$ 

(ref 64) and  $\Delta H_{f^{\circ}298}(C_2H_4) = 52.5 \pm 0.3 \text{ kJ mol}^{-1}$  (ref 59), we obtain  $\Delta H_{f^{\circ}298}(n\text{-}C_4H_9) = 84.1 \text{ kJ mol}^{-1}$ .

The uncertainty of this value can be estimated from the combined uncertainties in the heats of formation of  $C_2H_5$  and  $C_2H_4$ , in the value of  $E_1$ , and the uncertainty induced by possible errors in the  $k_{-1}^{\infty}(T)$  dependence used in developing the model of reaction 1,-1. The latter value is estimated as follows.

The "global" fitting (section IV.3) of our data on  $k_1(T,[He])$  (which are relatively close to the high-pressure limit) is most sensitive to the high-pressure limit rate constants at the temperatures of the experiments. Hence, if a different model of the transition state (and a different high-pressure preexponential factor) is used, this fitting procedure will try to compensate for the change of the preexponential factor by changing E<sub>1</sub> in order to get the same values of  $k_1^{\circ}$  at the temperatures of the experiments. In our data analysis, the vibrational frequencies of the transition state were selected to reproduce the temperature dependence of  $k_{-1}^{\circ}$ , formula III. This dependence is based on the recommendation of Kerr and Parsonage for  $k_{-1}/(k_7)^{0.5}$  and the  $k_7$  value recommended by Baulch et al.<sup>37</sup> The recommended<sup>37</sup> uncertainty factor for  $k_7$  is 10<sup>0.3</sup>, which yields an uncertainty factor of 1.4 for  $k_{-1}^{\circ}$ .

If values of  $k_{-1}^{\infty}$  changed by a factor of 1.4 are used in the "global" fitting procedure (section IV.3), a change of 1.7 kJ mol<sup>-1</sup> will be required in the value of  $E_1$  to obtain the same high-pressure limit rate constant of reaction 1 at 590 K, the average temperature of our experiments. We use twice this value (3.4 kJ mol<sup>-1</sup>) as a measure of the uncertainty in the thermochemistry induced by the uncertainty in the  $k_{-1}^{\infty}(T)$  dependence.

Combining this value with the uncertainties of  $E_1$  and the heats of formation of  $C_2H_5$  and  $C_2H_4$ , we obtain

$$\Delta H_{\rm f}^{\circ}{}_{298}(n-{\rm C_4}{\rm H_9}) = 84.1 \pm 4.2 \text{ kJ mol}^{-1}$$

and, using  $\Delta H_{f^{\circ}298}(n-C_4H_{10}) = -125.6 \pm 0.7 \text{ kJ mol}^{-1}$  (ref 63), we obtain the bond energy

$$DH_{208}(n-C_4H_9-H) = 427.7 \pm 4.3 \text{ kJ mol}^{-1}$$

Our  $\Delta H_{\rm f}^{\circ}{}_{298}(n\text{-}C_4\text{H}_9) = 84.1 \pm 4.2 \text{ kJ mol}{}^{-1} \text{ is } 3.6 \text{ kJ mol}{}^{-1}$  higher than the directly determined value of Seetula and Slagle<sup>34</sup> (80.5  $\pm$  2.2 kJ mol $^{-1}$  from the second-law treatment of the results on the kinetics of  $n\text{-}C_4\text{H}_9 + \text{HBr} \rightarrow n\text{-}C_4\text{H}_{10} + \text{Br}$  reaction). This disagreement lies within error limits 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.

7. Uncertainty in the  $\langle \Delta E \rangle_{\text{down}}^{\circ}$  and  $\langle \Delta E \rangle_{\text{all}}$  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 the collisional energy-transfer parameters,  $\langle \Delta E \rangle_{\text{down}}^{\circ}$  and  $\langle \Delta E \rangle_{\text{all}}$ . Since reaction (1,-1) is relatively close to its high-pressure limit at the conditions of these experiments, a small variation of the calculated values of  $k_1^{\infty}$  at these temperatures will noticeably affect the fitting parameters (i.e., the determinations of  $\langle \Delta E \rangle_{\text{down}}^{\circ}$ ). In the error assessment, we investigate the influence of the  $\pm 2.0 \text{ kJ} \text{ mol}^{-1}$  uncertainty in the barrier for the *n*-C<sub>4</sub>H<sub>9</sub> decomposition on the fitted values of  $\langle \Delta E \rangle_{\text{down}}^{\circ}$ .

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  $\pm 2.0$  kJ mol<sup>-1</sup>. This provided a change of  $k_1^{\infty}$  at 590 K, the average temperature of our experiments, of a factor

#### Decomposition of n-C<sub>4</sub>H<sub>9</sub> and iso-C<sub>4</sub>H<sub>9</sub> Radicals

of 1.5. The resulting individual calculated values of  $\langle \Delta E \rangle^{\circ}_{down}$  are significantly affected by these variations of the model. The fitted values of  $\langle \Delta E \rangle^{\circ}_{down}$  and  $-\langle \Delta E \rangle_{all}$  (in parentheses) are 328-(90)/125(14) cm<sup>-1</sup> (He) and 377(113)/146(20) cm<sup>-1</sup> (N<sub>2</sub>) with the lower values of  $\langle \Delta E \rangle^{\circ}_{down}$  corresponding to the lower value of the energy barrier.

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

$$-\langle \Delta E \rangle_{\text{all}} = 28 \binom{+62}{-14} \text{ cm}^{-1} \text{ for He as bath gas}$$
$$-\langle \Delta E \rangle_{\text{all}} = 40 \binom{+73}{-20} \text{ cm}^{-1} \text{ for N}_2 \text{ as bath gas}$$

or

$$\langle \Delta E \rangle^{\circ}_{\text{down}} = 184 \binom{+144}{-59} \text{ cm}^{-1}$$
 for He as bath gas  
 $\langle \Delta E \rangle^{\circ}_{\text{down}} = 215 \binom{+162}{-69} \text{ cm}^{-1}$  for N<sub>2</sub> as bath gas

at T = 560-620 K. These average values are comparable to the values for other alkyl radicals which have now been determined<sup>8-15</sup> by modeling the results of experiments of a similar type and which cover the range of values 130-360 cm<sup>-1</sup> for He as bath gas and 130-500 cm<sup>-1</sup> for N<sub>2</sub> as bath gas.

## V. Parametrization of Rate Constants

We present here a parametrization of  $k_1$  and  $k_2$  in helium and nitrogen which provides rate constant values throughout the range of temperatures 298–900 K and pressures 0.001–10 atm. The modified Lindemann–Hinshelwood expression introduced by Gilbert et al.<sup>65</sup> was used:

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

Values of  $k_1([M],T)$  and  $k_2([M],T)$  in the above temperature and pressure intervals were calculated using the master equation/ RRKM approach assuming  $\langle \Delta E \rangle_{all}$  independent of temperature for both bath gases. For reaction 1, the values of  $\langle \Delta E \rangle_{all}$ obtained from the modeling of experimental data ( $-28 \text{ cm}^{-1}$ in He and  $-40 \text{ cm}^{-1}$  in N<sub>2</sub>) were used. For reaction 2, the value of  $\langle \Delta E \rangle_{all} = -53 \text{ cm}^{-1}$  was used for both He and N<sub>2</sub>, which corresponds to  $\langle \Delta E \rangle_{\text{down}} = 250 \text{ cm}^{-1}$  at 600 K. The latter value was chosen based on the results of previous studies<sup>8-15</sup> of decomposition of hydrocarbon radicals. It results in the calculated value of  $k_2(650 \text{ K}, 4 \text{ Torr}) = 665 \text{ s}^{-1}$  in He which is in a qualitative agreement with our experimental observation made under these conditions: a fast decay of iso-C<sub>4</sub>H<sub>9</sub> was monitored but could not be measured quantitatively due to experimental complications (section II). The matrixes of calculated values of  $k_1(M,T)$  were fitted with the modified Lindemann-Hinshelwood expression X and the resulting parameters are

$$k_1^{\infty} = 1.06 \times 10^{13} \exp(-14005 \text{ K/T}) \text{ s}^{-1}$$
  
 $k_2^{\infty} = 2.14 \times 10^{12} T^{0.65} \exp(-15529 \text{ K/T}) \text{ s}^{-1}$ 

$$k_1^{\circ} = 3.82 \times 10^{31} T^{-11.94} \exp(-16292 \text{ K/T})$$
  
cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (reaction 1)

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$$F_{\text{cent}} = 1.53 \times 10^4 \exp(-10578 \text{ K/T}) + 0.190 \exp(205 \text{ K/T}) \text{ (reaction 1)}$$

$$k_2^{\circ} = 2.87 \times 10^{35} T^{-12.92} \exp(-18031 \text{ K/T})$$
  
cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (reaction 2)

$$F_{\text{cent}} = 103.2 \exp(-6762 \text{ K/T}) + 0.1186 \exp(242 \text{ K/T})$$
  
(reaction 2)

$$k_1^{\circ} = 3.15 \times 10^{31} T^{-11.91} \exp(-16237 \text{ K/T})$$
  
cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (reaction 1)

$$F_{\text{cent}} = 1.46 \times 10^4 \exp(-10565 \text{ K/T}) + 0.189 \exp(214 \text{ K/T}) \text{ (reaction 1)}$$

$$k_2^{\circ} = 1.05 \times 10^{35} T^{-12.85} \exp(-17900 \text{ K/T})$$
  
cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> (reaction 2)

$$F_{cent} = 470 \exp(-8187 \text{ K/T}) + 0.1269 \exp(470 \text{ K/T})$$
(reaction 2)

for nitrogen as bath gas.

The average deviation of the parametrized values of  $k_1$  and  $k_2$  from the master equation rate constants over this large range of conditions is 6%, with maximum deviation of 17%.

Recently, Bernshtein and Oref<sup>66</sup> demonstrated that the steadystate approximation cannot be used for calculation of unimolecular reaction rates by the master equation solution at high temperatures and low pressures, where relaxation to the steadystate population occurs on time scales comparable to the reaction time. The examples given by these authors indicate that reasonable agreement between the exact values of rate constants and those obtained under the steady-state assumption is reached after several hundred collisions with the bath gas. The calculations presented here are limited to conditions where the ratio of collision frequency to the rate constant is higher than 400. This requirement and the pressure range of 0.001-10 atm determine the upper temperature limit (900 K) of the current parametrization. For the low-pressure limit rate constant expressions, however, the upper temperature limit determined by this requirement is lower-820 K.

Due to the uncertainty in the parameters of the models discussed above and in the temperature dependence of  $\langle \Delta E \rangle_{\rm down}$  caution is advised in using the results of this extrapolation.

#### VI. Summary

The unimolecular decomposition of  $n-C_4H_9$  in helium and nitrogen (reaction 1) 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 calculate k(E) values for the master equation analysis. The experimental values of  $k_1$  were reproduced by master equation/RRKM modeling.

Literature data on the reaction  $iso-C_4H_9 \rightarrow CH_3 + C_3H_6$  (2,-2) were reanalyzed and a transition-state model of this reaction was developed which provides the high-pressure limit rate constants. Finally, parametrized expressions are presented which provide values of  $k_1$  and  $k_2$  over a wide range of pressures and temperatures.

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**Supporting Information Available:** Tables 1S-3S containing information on the properties of *n*-butyl and *iso*-butyl radicals and corresponding transition states obtained in the ab initio study (5 pages). Ordering information is given on any current masthead page.

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