Unimolecular Decomposition of t-C₄H₉ Radical

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The kinetics of the unimolecular decomposition of the $t-C_4H_9$ radical has been studied. The reaction was isolated for quantitative study 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 (712-779 K) and bath gas density $((3-22) \times 10^{16} \text{ molecules cm}^{-3})$ in He. The rate constants are in the falloff region under the conditions of the experiments. A transition-state model was created to obtain values of the microcanonical rate constants, k(E), needed to solve the master equation. The transition-state model provides the high-pressure limit rate constants for the decomposition reaction $(k_1^{\circ}(t-C_4H_9 \rightarrow i-C_4H_8 + H) = 2.18 \times 10^{\circ}$ $10^9 T^{1.48} \exp(-18120 \text{ K/T}) \text{ s}^{-1}$ and the reverse reaction $(k_{-1}^{\infty}(\text{H} + i\text{-}C_4\text{H}_8 \rightarrow t\text{-}C_4\text{H}_9) = 1.03 \times 10^{-11} T^{0.25}$ $\exp(-737 \text{ K}/T) \text{ cm}^3$ molecule⁻¹ s⁻¹). The results of earlier studies of reactions of decomposition of t-C₄H₉ and the reverse reaction which reported the value of the enthalpy of formation of t-C₄H₉ were reanalyzed, and the resultant value of $\Delta H_{f}^{o}_{298}(t-C_{4}H_{9})$ is in agreement with the most current measurements. The falloff behavior was analyzed using a master equation approach. The hindered internal rotations of methyl groups in the involved molecules were treated classically. Simple formulas for the density-of-states and sum-of-states functions of a one-dimensional hindered rotor based on the inverse Laplace transform of the classical partition function are reported. The average value of $\langle \Delta E \rangle_{down} = 230 \text{ cm}^{-1}$ for the energy loss probability was obtained using the 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 and N₂ is provided using the modified Lindemann-Hinshelwood expression.

I. Introduction

The unimolecular decomposition of the alkyl radicals is an integral part of all high-temperature hydrocarbon pyrolysis and oxidation mechanisms.¹⁻³ Knowledge of kinetics of these reactions is essential for accurate modeling of the physical and chemical behavior of flames and other combustion systems.^{4,5} Most of our current knowledge of the behavior of these unimolecular reactions (rate constants, falloff characteristics, etc.) 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 high-temperature chemical processes.

We have recently developed an experimental procedure 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.^{7,8} Rate constants are measured as a function of temperature and bath-gas density. Falloff behavior is analyzed using the master equation approach to characterize weak-collision effects. It has been possible in favorable cases to obtain not only a temperatureaveraged value of $\langle \Delta E \rangle_{down}$, 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 dependences 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: $HCO,^7 n-C_5H_{11},^8 C_2H_5,^9 i-C_3H_7,^{10} n-C_3H_7,^{11} CH_3CO,^{12}$ and $CH_3CHCl.^{13}$

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

$$t - C_4 H_9 \rightleftharpoons i - C_4 H_8 + H$$
 (1, -1)

Rate constants for reaction 1 were measured at five bath-gas (helium) densities between 712 and 779 K. Data analysis required characterizing a transition-state model which, when used in RRKM calculations, reproduces the reported high-pressure-limit rate constants of reactions 1 and -1 including the temperature dependences. This same transition-state model is used to provide k(E) values needed in the master equation analyses of the weak-collision effects as manifested in the observed falloff behavior of the measured rate constants.

In the RRKM calculations, account must be taken of the states of the internal CH₃ rotors. This problem is particularly important in the case of the t-C₄H₉ radical where there are three such rotors. We demonstrate the appropriateness of using the classical expression¹⁴ for the partition function for these rotors in RRKM and equilibrium constant calculations. Use of the classical approximation makes it possible to obtain simple, accurate expressions for the sum of states and density of states functions of the one-dimensional hindered internal rotors. Such expressions are presented here.

The unimolecular decomposition of the t-C₄H₉ radical has not been isolated for direct study before. Rate constant ratios of reaction 1 relative to the t-C₄H₉ + t-C₄H₉ reaction derived from the kinetics of complex systems are available and have been analyzed by Tsang⁶ to provide absolute rate constants of k_1 . Rate constants for reaction 1 so derived from the results of Canosa and Marshall¹⁵ in the range 584–604 K at pressures (of i-C₄H₁₀) up to 272 Torr appear to be high-pressure limit results. Another determination of such ratios has been reported by Birrell and Trotman-Dickenson¹⁶ at lower pressure (\approx 40 Torr of (CH₃)₃-CCHO bath gas) and higher temperatures (\leq 797 K) where k_1 is in the falloff region.

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The kinetics of the reverse reaction, the addition of H atoms to isobutene, has been investigated by three groups at lower temperatures than those that were used to study the forward reaction. The results of Harris and Pitts¹⁷ (301-441 K) and of Canosa et al.¹⁸ (298-563 K) are in excellent agreement. Those obtained by Kyogoku et al.¹⁹ (225-438 K) agree with the results of the other two studies only near 400 K, the highest temperature of the latter study.

II. Experimental Study

Details of the experimental apparatus²⁰ and procedures⁸ used have been described before and so are only briefly reviewed here. The *tert*-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 193-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 boric acid. Gas flowing through the tube at ≈ 4 m s⁻¹ contained the radical precursor (<0.1%) and the inert carrier gas (He) in large excess (>99.9%). The flowing gas was completely replaced between laser pulses.

The tert-butyl radicals were produced by the pulsed, 193-nm laser photolysis of pinacolone

$$(CH_3)_3CC(O)CH_3 \xrightarrow{193 \text{ nm}} t \cdot C_4H_9 + \text{ other products}$$
 (2)

or 2,2,4,4-tetramethyl-3-pentanone

$$(CH_3)_3CC(O)C(CH_3)_3 \xrightarrow{193 \text{ nm}} t - C_4H_9 + \text{ other products}$$
 (3)

The nature of the radical precursor had no influence on the observed kinetics of the *tert*-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 t-C₄H₉ + t-C₄H₉) had negligible rates compared to that of the unimolecular decomposition of the t-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. *tert*-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 (pinacolone, 98%; 2,2,4,4-tetramethyl-3-pentanone, 99%) and Matheson (He, >99.995%). Precursors were purified by vacuum distillation prior to use. The helium was used as provided.

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

Unimolecular decay of $t-C_4H_9$ was observed only above 660 K. Below this temperature a slow decay of $t-C_4H_9$ is observed due to a first-order heterogeneous wall-loss process:

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

 k_4 is significant at ambient temperature ($\approx 200 \text{ s}^{-1}$) but decreases monotonically with increasing temperature reaching an asymptotic value of 25-60 s⁻¹ at 600 K. At temperatures between 600 and 660 K, just below the temperature of this study, k_4 appears to be independent of temperature.

Above 660 K the decay constant increased rapidly with rising temperature due to the increasing importance of the thermal decomposition of the *tert*-butyl radical, reaction 1. The *t*-C₄H₉ decay constants were analyzed assuming that the *tert*-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 660 K the sum of the two loss processes is observed ($k' = k_1 + k_4$).

Sets of experiments were conducted as a function of temperature using five different fixed helium densities in the range $(3-22) \times 10^{16}$ molecules cm⁻³ to determine k_1 as a function of these variables. The lower limit of pressures used was determined by the sensitivity of the radical detection system. The upper limit was determined by the need to maintain low pressure in the mass spectrometer. In each set of experiments the *t*-C₄H₉ exponential decay constant, k', was measured as a function of temperature keeping the concentration of all gases constant.

Calculations of k_1 from measurements of k'require knowledge of k_4 above 660 K. While k_4 was directly determined below 660 K, it could not be measured above this temperature due to the additional loss of radicals by unimolecular decomposition. As stated above, between 600 and 660 K, k_4 was directly determined, and it was found to be temperature independent. Values of k_4 above 660 K needed to determine k_1 from the measurements of k' were obtained by an extrapolation assuming that k_4 retains this temperature independence beyond 660 K up to the highest temperature of this study, 779 K. To minimize possible errors in the determination of k_1 caused by this assumed temperature independence of k_4 above 660 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. Other butyl radical isomers are expected to decompose at significantly lower temperatures than the *tert*-butyl radicals since they decompose by a lower energy process, C-C bond cleavage. For example, we observe the decomposition of *sec*- C_4H_9 radicals experimentally²¹ in the temperature interval from 610 to 670 K at He densities from 3×10^{16} to 20×10^{16} molecules cm⁻³. No signs of radical decomposition were detected in the current study at temperatures below 660 K, indicating an absence of C_4H_9 isomers other than *t*- C_4H_9 .

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 Figure 1. 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.

Classical failoff curves, k_1 vs [He], for seven temperatures near those actually used in the experiments are displayed in Figure 2. The displayed values of k_1 at these temperatures were obtained from the Arrhenius fits of experimental rate constants obtained at fixed densities of He, those displayed in Figure 1.

TABLE 1: Conditions and Results of Experiments To Measure the Unimolecular Rate Constants (k_1) of the Thermal Decomposition of *tert*-Butyl Radicals

10 ⁻¹⁶ [M]	T	10-13[precursor]	<i>k</i> 4	k_1	master equation analysis
(molecules cm ⁻³)	<u>(K)</u>	(molecules cm ⁻³)	(s ⁻¹)	(s ⁻¹)	$(\Delta E)_{\rm down} (\rm Cm^{-1})$
3.0	757	1.4	52.3	157	281
3.0	769	1.4	52.3	199	267
3.0	779	1.4	60.3	252	268
6.0	731	1.3	38.6	89.2	215
6.0	738	0.67	44.6	120	241
6.0	740	1.3	38.6	116	219
6.0	740	0.67	44.4	126	239
6.0	749	3.5ª	66.4	154	230
6.0	749	3.5ª	65.1	152	227
6.0	750	1.3	38.6	160	233
6.0	761	1.3	48.3	210	232
6.0	761	3.5ª	66.4	209	231
6.0	761	3.54	65.1	217	240
6.0	770	0.67	44.4	315	282
6.0	779	1.4	60.3	391	282
12.0	718	0.85	38.7	79.5	195
12.0	731	0.84	38.7	132	227
12.0	739	4.3ª	57.7	164	225
12.0	739	4.34	50.9	157	214
12.0	741	0.84	38.7	176	229
12.0	750	14	32.8	238	246
12.0	751	4 34	57.7	221	219
12.0	751	4.30	50.9	231	230
12.0	759	14	45.9	314	258
12.0	761	4 34	577	316	230
12.0	761	4.3	50.0	318	244
12.0	770	1.5	45 0	434	270
12.0	721	1.7	143	111	210
18.0	721	1.2	41 G	00.2	192
18.0	720	0.63	40.5	127	105
18.0	730	0.03	47.5	141	190
18.0	730	0.03	42.0	141	203
18.0	733	1.2	44.3	100	223
18.0	741	1.2	44.3	212	229
18.0	741	0.63	49.5	209	225
18.0	741	0.03	42.0	210	235
10.0	751	1.3	44.0	200	230
18.0	/01	1.3	20.0	304	230
22.0	/12	1.3	38.8	/9.3	1/4
22.0	720	1.3	38.8	106	184
22.0	/30	1.4	40.6	16/	225
22.0	/30	1.4	40.2	162	216
22.0	731	1.3	38.8	141	176
22.0	740	1.3	49.7	243	253
22.0	740	1.4	40.2	226	230
22.0	751	1.4	49.7	297	221
22.0	762	1.4	58.6	426	240

^a 2,2,4,4-Tetramethyl-3-pentanone was used as radical precursor. Pinacolone was used in all other experiments.



Figure 1. Plot of t-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 apparent temperature dependence of $\langle \Delta E \rangle_{down}$ ($\langle \Delta E \rangle_{down} = 1.32T - 757$ cm⁻¹).

The only product of reaction 1 observed in the present study had a mass corresponding to C_4H_8 and a rate of formation



Figure 2. Falloff curves, k_1 vs [He], for six temperatures near those actually used in the experiments. The displayed values of k_1 at these temperatures were calculated from the Arrhenius fits of experimental rate constants obtained at fixed densities of He as displayed in Figure 1.

appearing to match that of t-C₄H₉ decay. C₄H₈ is also a product of the heterogeneous reaction, and thus it was not possible to confirm reaction 1 as a source of C₄H₈. No formation of CH₃ was detected.

III. Data Analysis

Weak-collision effects in reactions 1 and -1 (falloff from the high-pressure limit) were analyzed using master equation modeling. In this section knowledge of the high-pressure limit rate constants $(k_1^{\infty}, k_{-1}^{\infty})$ is first reviewed. Then, a transition-state model is created which reproduces the high-pressure limit rate constants $k_1^{\infty}(T)$ and $k_{-1}^{\infty}(T)$. This transition-state model provides the values of the microcanonical rate constants, k(E). needed in the master equation modeling. The density of states and sum of states functions of the tert-butyl 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, and formulas for the density of states and sum of states functions are developed using the inverse Laplace transform of the classical partition functions. Finally, the experimental rate constants (falloff from the high-pressure limit) are reproduced by master equation/RRKM modeling in order to obtain quantitative information on the weak-collision effects in reactions 1 and -1.

1. Experimental High-Pressure Limit Rate Constants of Reactions 1 and -1. There are three published studies on the kinetics of reaction -1, the association of H atoms with isobutene.¹⁷⁻¹⁹ All were conducted under pseudo-first-order conditions using an excess of $i-C_4H_8$. Canosa et al.¹⁸ used a discharge flow reactor and mass spectrometry for species detection. Conditions covered include pressures of 7-8 Torr and temperatures in the range 298-563 K. Harris and Pitts¹⁷ used flash photolysis to produce the H atoms and resonance fluorescence to detect the atoms. They worked at 298 K < T < 441 K and pressures in the range 50-100 Torr. Kyogoku et al.¹⁹ employed pulsed radiolysis to produce H atoms and detected them using Lyman- α absorption between 200 and 500 K and at 600 Torr total pressure. The results of the first two studies, those of Canosa et al. and Harris and Pitts, are in excellent agreement (see Figure 3). However, there is disagreement between the results of these two studies and that of Kyogoku et al. All studies appear to be conducted at the



Figure 3. Plot of experimental (symbols) and calculated (lines) values of k_1° and k_{-1}° vs 1000/T. (a) Plot of k_{-1}° vs 1000/T: Canosa et al. (ref 18), Harris and Pitts (ref 17), Kyogoku et al. (ref 19). (b) Plot of k_1° vs 1000/T: Birrell and Trotman-Dickenson (ref 16), Canosa and Marshall (ref 15). Lines are from the TST calculations using the model described in text, section III.2.

high-pressure limit of reactions 1 and -1. We adopt the results of Harris and Pitts as the most accurate measure of k_{-1}^{∞}

$$k_{-1}^{\infty} = (6.11 \pm 0.6) \times 10^{11} \times \exp(-(7.06 \pm 0.82) \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (\text{I})$$

since this study employed the most sensitive method for detection of H atoms and thus could best avoid the influence of secondary reactions.

Although there are other possible channels in the reaction between H atoms and isobutene besides reaction -1, none is expected to contribute significantly to the overall rate at the conditions of experiments by Harris and Pitts.^{22,23}

There are two experimental studies of reaction 1 available in the literature.^{15,16} Both are relative rate constant measurements which determined the ratio $k_1/k_s^{1/2}$, where k_5 is the rate constant of recombination of *tert*-butyl radicals:

$$2t \cdot C_4 H_9 \rightarrow (CH_3)_3 CC(CH_3)_3$$
(5)

Using the recommended expression for k_{5} ,^{24,25}

$$k_5 = 4 \times 10^{-12} (300 \text{ K}/T)^{1.5} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

we obtain the values of k_1 which are shown in Figure 3. The displayed error limits of k_1 reflect an uncertainty factor of 2 in k_5 suggested by Tsang.²⁵

While the results of Canosa and Marshall¹⁵ are at the highpressure limit (up to 272 Torr of C₄H₁₀), those of Birrell and Trotman-Dickenson¹⁶ are in the falloff region. The latter experiments were conducted at pressure of \approx 40 Torr of pivaldehyde at temperatures 666 K $\leq T \leq$ 797 K.

2. Transition-State Model of Reactions 1 and -1. A transitionstate model of reactions 1 and -1 was developed which can reproduce the magnitude and temperature dependence of k_1^{∞} and k_{-1}^{∞} . This same transition-state model is later used to provide k(E) values in the master equation analysis of the weak-collision effects in reactions 1 and -1. k_{-1}^{∞} is given by²⁶

$$k_{-1}^{\infty} = \frac{k_{\rm B}T}{h} \frac{Q^{\rm t}}{Q_{\rm H}Q_{\rm C_4H_8}} \exp\left(-\frac{\Delta E^{\rm 0}_{-1}}{k_{\rm B}T}\right)$$

where Q^{\ddagger} , Q_{H} , and $Q_{C_{4}H_{3}}$ are partition functions of the transition state, H atom, and isobutene molecule, respectively, and ΔE^{0}_{-1} is the energy barrier height for association.

Calculation of k_{-1}^{∞} requires knowledge of the structure and vibrational frequencies of the isobutene molecule. The geometric structure of isobutene is known.²⁷ Listings of vibrational frequencies of isobutene were published by Shimanouchi²⁸ and Luttke and Braun.²⁹ The reported values are very close to each other but do differ in the value assigned to the (a_2) CH₂ twist: 981²⁸ or 697 cm⁻¹.²⁹ Ab initio calculations by Guo and Karplus³⁰ favor the latter value. Hence, we have chosen to use the set of vibrational frequencies reported by Luttke and Braun. The barrier height for internal rotations (8.7 kJ mol⁻¹) was taken from Durig et al.³¹ The partition functions of one-dimensional hindered rotations used in the TST calculations of the high-pressure limit rate constants were calculated using an appropriate classical expression¹⁴ (see below).

There exists an addition barrier in reaction -1. Hence, the transition state is tight, and the moments of inertia of the transition state and *tert*-butyl radical do not differ significantly. They were taken to be equal in the model. The barrier heights for the one-dimensional internal rotations of two methyl groups in the transition state (7.5 kJ mol⁻¹) were taken as the average of those for isobutene and the *tert*-butyl radical. The two lowest vibrational frequencies of the transition state and the *add*ition energy barrier height for the association reaction ΔE^{0}_{-1} were varied to fit the calculated high-pressure limit rate constants of reaction -1 to the Arrhenius expression I at temperatures in the range 298–441 K. Frequencies and other parameters of the transition state obtained through this fitting procedure are listed in Table 2.

The structure and frequencies of the *tert*-butyl radical were taken from ab initio calculations by Pacansky et al.^{33,34} Although many of the vibrational frequencies of $t-C_4H_9$ were measured experimentally, there is still significant uncertainty in the value of the low frequency of the pyramidal bending motion. It was suggested earlier³⁵ that this frequency is lower than 200 cm⁻¹, because otherwise it should have been experimentally detected along with other vibrational transitions.³⁵ However, the most recent ab initio study by Pacansky et al.³³ gave the value of 282 cm⁻¹ at the UMP2/6-31G* level. Another possible explanation³³ for the failure to detect this transition is its possibly low intensity, although ab initio calculations predict an intensity high enough for detection. We chose to use the self-consistent set of calculated parameters for the *tert*-butyl radical reported by Pacansky et al.³³

Reduced moments of inertia for the one-dimensional internal methyl rotors for both *tert*-butyl radical and isobutene were calculated from the structural data using the method of Pitzer and Gwinn.¹⁴ All molecular parameters of the *tert*-butyl radical, isobutene, and the transition state used in current study are listed in Table 2. The thermodynamic functions of the *t*-C₄H₉ radical calculated using the above model are listed in Table 3.

One test of the appropriateness of the selected parameters of the *tert*-butyl radical is to compare the calculated entropy with the value obtained from experiment. The room temperature entropy for the *tert*-butyl radical was calculated assuming separability of vibrational and rotational (including internal) degrees of freedom and using the values of Pitzer and Gwinn¹⁴ for thermodynamic functions of the hindered internal rotors. The calculated value of $S^{\circ}_{298} = 314.0 \text{ J mol}^{-1} \text{ K}^{-1}$ coincides with the value obtained in the recent experimental study of Seakins et al.,³⁶ 313 ± 5 J mol⁻¹ K⁻¹.

TABLE 2: Molecular Parameters of $t-C_4H_9$, $i-C_4H_8$, and Transition State $(t-C_4H_9^{\ddagger})$

	Vibrational Frequencies (cm ⁻¹))					
t-C₄H9	3187(2), 3136(2), 3038(2), 1562(2),	1539(2), 1462(2),					
	1351(2), 1050(2), 974(2), 388(2),	, 3137, 3043, 1557,					
	1485, 1157, 793, 282, 3183, 1540,	1001					
I-C4H8	2981, 2970, 2909, 1660, 1445, 1430, 382, 2930, 1452, 1070, 697, 3087	1381, 1062, 804,					
	1366, 1281, 980, 895, 428, 2946, 1	455, 1121, 888, 418					
t-C₄H₀ [‡]	3040(8), 1550(6), 1470(3), 1350(2),	1100(3), 970(2),					
	400(2), 900, 700, 200, 170						
Overall Rotations: Rotational Constants (cm ⁻¹) and Symmetry Numbers							
t-C₄H₀	$(ABC)^{1/3} = 0.219; \sigma$	= 3 (inactive)					
i-C4H8	$(ABC)^{1/3} = 0.237; \sigma$	= 2 (inactive)					
t-C ₄ H ₉ ‡	$(ABC)^{1/3} = 0.219; \sigma$	= 1 (inactive)					
Methyl Gr Symr	The second seco	Constants (cm ⁻¹), rs (kJ mol ⁻¹) 6.3 8.7 7.5					
Lennard-Jones Parameters ^a							
gas	ϵ/k (K)	σ (Å)					
He	10.22	2.551					
N_2	71.4	3.798					
t-C ₄ H ₉ t	330.1	5.278					
^a Taken from	m ref 32. ^b Taken to be the same a	s for <i>i-</i> C4H10.					

The barrier to dissociation of the $t-C_4H_9$ radical was obtained from the known energetics of the system and the transition-state model. The heat of formation of *tert*-butyl radical was taken from ref 36: $\Delta H_1^{\circ}_{298}(t-C_4H_9) = 51.3 \pm 1.7 \text{ kJ mol}^{-1}$. The heat of formation of isobutene is $\Delta H_{f}^{\circ}_{298}(i-C_{4}H_{8}) = -16.9 \pm 0.6 \text{ kJ}$ mol⁻¹,³⁷ and the fitted value for the barrier for addition $\Delta E_{-1}^{0} =$ 6.22 kJ mol⁻¹ results in a value of $\Delta E^{0}_{1} = 152.6$ kJ mol⁻¹ for the dissociation energy barrier. Since hindered internal rotations in $t-C_4H_9$, isobutene, 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 tert-butyl radical has an overall rotational symmetry factor of 3 and three internal rotors with symmetry factors of 3 each-total symmetry factor 81. The transition state has no overall rotational symmetry and two internal rotors with symmetry factors of 3 each-total symmetry factor 9. Hence,²⁶ the decomposition reaction has a reaction path degeneracy of 9.

The model of the transition state of reactions 1 and -1 described above results in the following expressions for high-pressure limit rate constants of reactions 1 and -1 at 298 K < T < 1500 K:

$$k_1^{\infty} = 2.18 \times 10^9 T^{1.48} \exp(-18120 \text{ K}/T) \text{ s}^{-1}$$
 (II)

$$k_{-1}^{\infty} = 1.03 \times 10^{-11} T^{0.25} \times \exp(-737 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (III)

These Arrhenius expressions are plotted in Figure 3 together with the experimental determinations. The expression for the association rate constant k_{-1} is in agreement with the results of Harris and Pitts¹⁷ and of Canosa et al.,¹⁸ as expected.

Tsang⁶ recommended two expressions for k_1^{∞} based on his analysis of the results of Canosa and Marshall¹⁵ and of Birrell and Trotman-Dickenson:¹⁶

$$k_1^{\infty} = 8.3 \times 10^{13} \exp(-18895 \text{ K/T}) \text{ s}^{-1}$$
 (IVa)

if the internal rotations in $t-C_4H_9$ are free

$$k_1^{\infty} = 1.58 \times 10^{14} \exp(-19364 \text{ K}/T) \text{ s}^{-1}$$
 (IVb)

if the internal rotations in $t-C_4H_9$ have barriers of 10 kJ mol⁻¹. The rate constant values provided by formulas IVa and IVb recommended by Tsang are, on the average, lower than those

provided by formula II by 33% (formula IVa) and 43% (formula IVb) at T = 298-1500 K.

The results of Canosa and Marshall¹⁵ (k_1^{∞}) are reproduced by expression II within the error limits. The determinations of k_1 of Birrell and Trotman-Dickenson¹⁶ are in the falloff region. All their experiments were conducted at a pressure of ≈ 40 Torr of pivaldehyde at temperatures 666 K $\leq T \leq 797$ K. One would expect the measured rate constants to lie below k_1^{∞} and to exhibit a lower activation energy than that of k^{∞}_1 . While their k_1 values do lie below k_1^{∞} , their activation energy is not lower but rather is higher. These data are not regarded as reliable for obtaining additional values of k_1^{∞} .

3. Density-of-States Function for a 1-Dimensional Hindered Rotor. Inverse Laplace Transform of the Classical Partition Function. For modeling of the falloff behavior of reactions 1 and -1, knowledge is required of the density of states function of the *tert*-butyl radical and of the sum-of-states function of the transition state. The established common approach is to assume separability of vibrational and rotational degrees of freedom, as well as separability of the rotations of the molecule, internal and external.²⁶ Next, a model of the molecule consisting of harmonic oscillators and independent free rotors is developed. The densityof-states and sum-of-states functions of such a system can easily be calculated using the modified Beyer–Swinehart approach.³⁸ However, the *tert*-butyl radical presents a special case because of the presence of several one-dimensional hindered methyl rotors: three in the radical itself and two in the transition state.

One possible approach to the hindered rotor treatment is to solve the appropriate quantum-mechanical problem either exactly^{14,39} or using a semiclassical approximation.⁴⁰ These timeconsuming procedures involve determination of the energy levels of the hindered rotor and then direct counting of states. We propose here a different approach which results in simple formulas which can easily be incorporated in any program which handles density-of-states and sum-of-states functions.

In this section we present a formalism based on the inverse Laplace transform of the classical partition function which allows one to calculate density-of-states and sum-of-states functions of a one-dimensional hindered rotor. After that these functions for the whole molecule are calculated by numerical convolution. The described approach retains the assumption of separability of degrees of freedom and provides easy-to-use expressions.

The partition function of any system can be considered as a Laplace transform of the corresponding density-of-states function by definition:

$$Q(\beta) = \int_0^\infty \rho(E) e^{-\beta E} dE = L[\rho(E)]$$

where $\beta = (k_{\rm B}T)^{-1}$, E is the energy, and $\rho(E)$ is the density-ofstates function. Thus, provided that the formula for the dependence of the partition function Q on temperature T is known, one can obtain the density-of-states function by inverse Laplace transform (ILT):⁴¹

$$\rho(E) = L^{-1} \left[Q(\beta) \right]$$

This method of calculating the density-of-states function was applied by Robertson and Wardlaw⁴² to the propene molecule and the isopropyl radical. In that study an exact analytical expression was derived for the rotational kinetic energy of these molecules, including the terms describing the coupling between external and hindered internal rotations. Then formulas for the rotational partition functions were obtained, and ILT of those provided the density-of-states functions for both molecules considered. The formulas obtained in their study are molecule-specific, and new mathematical derivations are required if other molecules are to be considered.

TABLE 3: Thermodynamic Properties⁴ of t-C₄H₉

<i>T</i> (K)	C_p° (J mol ⁻¹ K ⁻¹)	S° (J mol ⁻¹ K ⁻¹)	$-(G^{\circ} - H_0^{\circ})/T (\text{kJ mol}^{-1})$	$H^{\circ} - H_0^{\circ} (\text{kJ mol}^{-1})$	$\Delta H_{\rm f}^{\circ}$ (kJ mol ⁻¹)	$\Delta G_{\rm f}^{\circ}$ (kJ mol ⁻¹)	$\log K_{\rm f}$
100	57.09	234.20	192.42	4.18	64.83	87.11	-45.50
200	76.74	280.82	225.76	11.01	58.23	112.01	-29.25
298.15	91.14	314.01	249.53	19.22	51.30	139.86	-24.50
300	91.46	314.57	249.93	19.39	51.17	140.41	-24.45
400	109.90	343.34	269.78	29.43	44.03	171.22	-22.36
500	129.24	369.98	287.18	41.40	37.55	203.79	-21.29
600	147.30	395.11	303.15	55.18	31.83	237.55	-20.68
700	163.39	419.07	318.01	70.74	27.09	272.23	-20.31
800	177.63	441.86	332.05	87.85	23.22	307.55	-20.08
900	190.25	463.52	345.44	106.27	20.12	343.30	-19.92
1000	201.37	484.15	358.27	125.88	17.72	379.37	-19.82
1100	211.16	503.80	370.61	146.52	15.90	415.64	-19.74
1200	219.74	522.55	382.48	168.09	14.62	452.05	-19.68
1300	227.26	540.45	393.94	190.47	13.76	488.55	-19.63
1400	233.89	557.54	405.02	213.53	13.22	525.10	-19.59
1500	239.69	573.88	415.73	237.21	12.97	561.68	-19.56

^a $\Delta H_{\rm f}^{\circ}$ at 298.15 K is taken from ref 36.

The approach of Robertson and Wardlaw can provide an exact classical rotational density-of-states function for any molecule as a whole. However, for RRKM calculation of energy-specific rate constants, k(E), the density of states of only active degrees of freedom is required, with two or three external rotations excluded.²⁶ Again, separability of degrees of freedom is assumed, so only formulas for an isolated 1-dimensional hindered rotor are needed.

The potential energy function of a 1-dimensional hindered internal rotor is traditionally approximated by a sinusoidal function:¹⁴

$$V = (V_0/2)[1 - \cos(\sigma\varphi)]$$

where σ is the number of potential minima, which usually coincides with the symmetry number of the rotor, φ is the torsional rotation angle, and V_0 is the barrier height. The classical partition function for such a potential can be written as¹⁴

$$Q_{\rm h}(\beta) = \frac{1}{\sigma} \left(\frac{\pi}{B\beta}\right)^{1/2} e^{-V_0 \beta/2} I_0\left(\frac{V_0 \beta}{2}\right) = Q_{\rm f}(\beta) e^{-V_0 \beta/2} I_0\left(\frac{V_0 \beta}{2}\right)$$
(V)

where Q_f is the partition function of the corresponding free rotor, *B* is the rotational constant, and I_0 is the modified Bessel function.⁴³ Since

$$L^{-1}[Q_{\rm f}(\beta)] = L^{-1}\left[\frac{1}{\sigma}\left(\frac{\pi}{B\beta}\right)^{1/2}\right] = \frac{1}{\sigma}(BE)^{-1/2}$$

and

$$L^{-1}\left[e^{-V_0\beta/2}I_0\left(\frac{V_0\beta}{2}\right)\right] = \frac{u(E) - u(E - V_0)}{\pi(E(V_0 - E))^{1/2}}$$

using the convolution rule, 43 we can obtain for the density-ofstates of a hindered internal rotor:

$$\rho(E) = \frac{1}{\sigma \pi B^{1/2}} \int_0^E \frac{[u(x) - u(x - V_0)] \, \mathrm{d}x}{(x(E - x)(V_0 - x))^{1/2}}$$
(VI)

where u(x) is a Heaviside step function.

In order to evaluate this integral, two cases should be considered: 1. $E > V_0$. In this case eq VI reduces to

$$\rho(E) = \frac{1}{\sigma \pi B^{1/2}} \int_0^{V_0} \frac{\mathrm{d}x}{\left(x(E-x)(V_0-x)\right)^{1/2}} \qquad (\text{VII})$$

which can be expressed via a corresponding elliptic integral⁴⁴

$$\rho(E) = \frac{2\mathbf{K}((V_0/E)^{1/2})}{\pi\sigma(BE)^{1/2}}$$

where K(x) is the complete elliptic integral of the first kind.^{43,44} 2. $E < V_0$. In this case eq VI reduces to

$$\rho(E) = \frac{1}{\sigma \pi B^{1/2}} \int_0^E \frac{\mathrm{d}x}{(x(E-x)(V_0-x))^{1/2}}$$

which is analogous to eq VII, but with E and V_0 changing positions. We thus obtain for this case

$$\rho(E) = \frac{2K((E/V_0)^{1/2})}{\pi\sigma(BV_0)^{1/2}}$$
(VIII)

Using formulas VII and VIII, we can now obtain expressions for the corresponding sum-of-states of the hindered internal rotor:

$$W(E) = \int_0^E \rho(E') \, \mathrm{d}E'$$

Again, two cases should be considered: 1. $E < V_0$.

$$W(E) = \frac{2}{\pi \sigma (BV_0)^{1/2}} \int_0^E K\!\left(\left(\frac{E'}{V_0}\right)^{1/2}\right) dE'$$

which can easily be evaluated

$$W(E) = \frac{4}{\pi\sigma} \left(\frac{V_0}{B}\right)^{1/2} \left[E\left(\left(\frac{E}{V_0}\right)^{1/2}\right) - \left(1 - \frac{E}{V_0}\right) K\left(\left(\frac{E}{V_0}\right)^{1/2}\right) \right]$$
(IX)

where E(x) is the complete elliptic integral of the second kind.^{43,44} 2. $E > V_0$.

$$W(E) = W(E=V_0) + \frac{2}{\pi\sigma(BV_0)^{1/2}} \int_{V_0}^E K\left(\left(\frac{V_0}{E'}\right)^{1/2}\right) \left(\frac{V_0}{E'}\right)^{1/2} dE'$$

taking $W(V_0)$ from (IX) and evaluating the integral, we obtain

$$W(E) = \frac{4}{\pi\sigma} \left(\frac{E}{B}\right)^{1/2} E\left(\left(\frac{V_0}{E}\right)^{1/2}\right)$$

Now we can present the summary of obtained formulas: Density-of-states function

$$\rho(E) = \begin{cases} \frac{2\mathbf{K}((E/V_0)^{1/2})}{\pi\sigma(BV_0)^{1/2}} & \text{for } E < V_0 \\ \frac{2\mathbf{K}((V_0/E)^{1/2})}{\pi\sigma(BE)^{1/2}} & \text{for } E > V_0 \end{cases}$$
(X)

sum-of-states function

$$W(E) = \begin{cases} \frac{4}{\pi\sigma} \left(\frac{V_0}{B}\right)^{1/2} \left[E\left(\left(\frac{E}{V_0}\right)^{1/2}\right) - \left(1 - \frac{E}{V_0}\right) K\left(\left(\frac{E}{V_0}\right)^{1/2}\right) \right] & \text{for } E \le V_0 \\ \frac{4}{\pi\sigma} \left(\frac{E}{B}\right)^{1/2} E\left(\left(\frac{V_0}{E}\right)^{1/2}\right) & \text{for } E > V_0 \end{cases}$$
(X1)

The limiting behavior of these functions coincides with those of the free rotor at $E \gg V_0$:

$$\lim_{(E/V_0) \to \infty} [\rho(E)] = \frac{2}{\pi \sigma(BE)^{1/2}} \lim_{(E/V_0) \to \infty} \left[K\left(\left(\frac{V_0}{E}\right)^{1/2}\right) \right] = \frac{1}{\sigma(BE)^{1/2}}$$

$$\lim_{E \to \infty} [W(E)] = \frac{1}{\sigma(BE)^{1/2}}$$

 $\lim_{(E/V_0)\to\infty} \left[V(E) \right]^{-2} \frac{4}{\pi\sigma} \left(\frac{E}{B} \right)^{1/2} \lim_{(E/V_0)\to\infty} \left[E\left(\left(\frac{V_0}{E} \right)^{1/2} \right) \right] = \frac{2}{\sigma} \left(\frac{E}{B} \right)^{1/2}$

and with those of corresponding harmonic oscillator with vibrational quantum size

$$h\nu = \sigma (BV_0)^{1/2}$$

at $E \ll V_0$

$$\lim_{(E/V_0)\to 0} [\rho(E)] = \frac{2}{\pi\sigma(BV_0)^{1/2}} \lim_{(E/V_0)\to 0} \left[K\left(\left(\frac{E}{V_0}\right)^{1/2}\right) \right] = \frac{1}{\sigma(BV_0)^{1/2}}$$
$$\lim_{(E/V_0)\to 0} [W(E)] = \frac{4}{\pi\sigma} \left(\frac{V_0}{B}\right)^{1/2} \left(\frac{\pi}{2} \frac{E}{V_0} - \lim_{(E/V_0)\to 0} \left[K\left(\left(\frac{E}{V_0}\right)^{1/2}\right) - E\left(\left(\frac{E}{V_0}\right)^{1/2}\right) \right] \right)$$
$$= \frac{E}{\sigma(BV_0)^{1/2}}$$

In 1977, Troe⁴⁵ suggested treating internal hindered rotors as harmonic oscillators at energies below the barrier and as free rotors at energies higher than barrier:

$$W(E) = \begin{cases} \frac{E}{\sigma(BV_0)^{1/2}} & E < V_0 \\ \frac{2}{\sigma} \left(\frac{E}{B}\right)^{1/2} & E > V_0 \end{cases}$$
(XII)

This approximation provides a jump by a factor of 2 in the value of the sum-of-states function at $E = V_0$ and an infinite value (δ -function) of the density-of-states function at this energy.

The energy dependence of the $\rho(E)$ and W(E) functions for the hindered internal rotor resulting from formulas X and XI, as well as from the approach suggested by Troe (formula XII),



Figure 4. Plot of density-of-states function (a) and sum-of-states function (b) vs reduced energy E/V of a one-dimensional hindered internal rotor obtained from ILT of classical partition function (formulas X and XI, solid lines) and from approach suggested in ref 45 (formula XII, dashed line). Note that density-of-states functions from both formulas have infinite values at E = V, where V is the barrier for internal rotation.

is presented in Figure 4. Note that, although the density-ofstates has an infinite value at $E = V_0$, the sum-of-states is finite, as is the partition function.

The limiting behavior of formula XII coincides with that of formula XI. However, as was noted by Troe,⁴⁵ it underestimates W(E) below the barrier and overestimates it above the barrier. This overestimation can amount to significant differences in integral characteristics, such as partition functions.

We compared the values of the rotational partition function calculated for the case of one internal methyl rotor in $t-C_4H_9$ radical with a barrier height value of 6.38 kJ mol⁻¹ (used in the current study) using the classical partition function (formula V) and that resulting from Troe's approach (formula XII) with the exact values obtained from tables in ref 14. Using formula XII results in an overestimation of the partition function up to 45% and a strong temperature dependence of this error, while use of formula V (or integration of formula X with the Boltzmann factor) gives an error of <5% at temperatures above 298 K.

The density-of-states (formula X) was calculated for each hindered internal rotor of the $t-C_4H_9$ radical separately. The total rotational density-of-states function was calculated by numerical convolution of these functions. An energy step size of 20 cm⁻¹ was used. The density-of-states of vibrational degrees of freedom was included using the modified Beyer–Swinehart algorithm.³⁸ It was verified that the total partition function of all active degrees of freedom (obtained by integration of the total density-of-states function) coincides with the exact value within 1.5% or better at the temperatures of the experiments and was within 5% over the broader temperature range 298 K < T < 1500 K. The sum-of-states function for the transition state was similarly calculated.

4. Master Equation Calculations of $k_1(T_{i}[M])$ and Determinations of $\langle \Delta E \rangle_{down}$. The measured rate constants of reaction 1 $(k_1(T, [M]))$ were reproduced using master equation simulations. The "exponential-down" model^{26,46,47} of collisional energy transfer was adopted to characterize the probability of deactivation of the t-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:

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



Figure 5. Plot of values of $\langle \Delta E \rangle_{\text{down}}$ vs temperature derived from the values of k_1 in Table 1. The line through the data is from the fit of the temperature dependence of $\langle \Delta E \rangle_{\text{down}} (\langle \Delta E \rangle_{\text{down}} = 1.32T - 757 \text{ cm}^{-1})$.

 $\langle \Delta E \rangle_{\text{down}}$ 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.^{26,41}

The method of Gaynor et al.^{26,48} for solving the master equation was employed. The energy bin size used in the fitting procedures was 20 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 1.5% of the exact values of the partition functions and rate constants at the temperatures of the experiments.

Falloff from the high-pressure limit is reproduced for each value of $k_1(T, [M])$ by the solution of the master equation using only $\langle \Delta E \rangle_{\text{down}}$ as an adjustable parameter. The results of these data fittings are presented in Table 1 and plotted vs T in Figure 5.

A temperature dependence of $\langle \Delta E \rangle_{\rm down}$ is apparent. Individual values displayed in Figure 5 were fitted to a linear function to give $\langle \Delta E \rangle_{\rm down} = 1.32T - 757$ cm⁻¹, which is indicated by the line in Figure 5.

A check of the quality of the model and data analysis procedure is provided by an inspection of the pressure dependence of $\langle \Delta E \rangle_{\rm down}$. The fitted values of $\langle \Delta E \rangle_{\rm down}$ should exhibit no dependence on pressure. Experiments to measure the rate constants of reaction 1 at the lower densities of bath gas were conducted, in general, at higher temperatures than the higherdensity experiments. Comparing individual values of $\langle \Delta E \rangle_{down}$ vs pressure involves comparing experiments conducted at different temperatures. To isolate the pressure dependence from the temperature dependence, the "reduced" function $\langle \Delta E \rangle_{\rm down}/(1.32T)$ -757 cm⁻¹) is used. This function vs pressure is plotted in Figure 6. The plot shows an absence of any pressure dependence which means that the model describes all sections of falloff in helium equally well in the range [He] = $(3-22) \times 10^{16}$ molecules cm⁻³. If the values of $\langle \Delta E \rangle_{\rm down}$ itself are plotted vs pressure, a slight bias toward lower values at higher pressures is visible. This bias, however, is well within the scatter of the individual data points.

5. Uncertainty in the $\langle \Delta E \rangle_{down}$ Determination in Reactions 1 and -1. There are sources of uncertainty in the energetics of reaction 1 which propagate into possible errors in the determination of $\langle \Delta E \rangle_{down}$. First is the heat of formation of the *t*-C₄H₉ radical. The value used here is from the recent study of Seakins et al.,³⁶ who report the value $\Delta H_f^{\circ}_{298}(t\text{-}C_4\text{H}_9) = 51.3 \pm 1.7 \text{ kJ}$ mol⁻¹. There are also uncertainties in the heat of formation of isobutene ($\Delta H_f^{\circ}_{298}(i\text{-}C_4\text{H}_8) = -16.9 \pm 0.6 \text{ kJ} \text{ mol}^{-1}$ ³⁷) and in the activation energy for reaction -1 ($E_{-1}^{\circ} = 7.06 \pm 0.82 \text{ kJ} \text{ mol}^{-1}^{-17}$).

Since reactions 1 and -1 are relatively close to their highpressure limit at the conditions of our experiments (k_1 is between



Figure 6. "Reduced" function $\langle \Delta E \rangle_{down}/(1.32T-757 \text{ cm}^{-1})$ vs pressure (see text, section III.4). The plot shows an absence of any pressure dependence which means that the model describes all sections of falloff in helium equally well in the range [He] = $(3-22) \times 10^{16}$ molecules cm⁻³.



Figure 7. Plot of values of $\langle \Delta E \rangle_{down}$ vs temperature derived from the values of k_1 in Table 1 using the modified model of reactions 1 and -1 (see text, section III.5). (a) Values obtained with barrier for decomposition changed by +3.1 kJ mol⁻¹; (b) values obtained with barrier for decomposition changed by -3.1 kJ mol⁻¹. The lines through the data are fits of the temperature dependences of $\langle \Delta E \rangle_{down}$.

7% and 25% of k_1^{∞}), small variation of the calculated values of k_1^{∞} at these temperatures will noticeably affect the fitting parameters (i.e., the determinations of $\langle \Delta E \rangle_{down}$). In this section we explore the propagation of these energy uncertainties, first in calculating k_1^{∞} (from k_{-1}^{∞} obtained from experiment) and then in $\langle \Delta E \rangle_{down}$. In the error assessment, all three uncertainties are combined and associated with an uncertainty in the energy barrier to dissociation, ΔE_1^0 , ± 3.1 kJ mol⁻¹, which comes from simply adding the uncertainties in the values of the heat of formation of *tert*-butyl radical and isobutene, and in the activation energy of the association reaction (-1).

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 ± 3.1 kJ mol⁻¹. This provided changes of k_1^{∞} at 750 K of -39% and +64%.

The resulting individual calculated values of $\langle \Delta E \rangle_{down}$ are significantly affected by these variations of the model. The average values of $\langle \Delta E \rangle_{down}$ changed from 230 cm⁻¹ obtained using the original model to 387 cm⁻¹ in the case of the higher barrier and 155 cm⁻¹ in the case of the lower barrier. In both cases $\langle \Delta E \rangle_{down}$ still showed a positive temperature dependence which can be fitted with linear function to give $\langle \Delta E \rangle_{down} = 0.770T -$ 186 cm⁻¹ for the higher barrier and $\langle \Delta E \rangle_{down} = 1.24T - 769$ cm⁻¹ for the lower barrier (Figure 7). The scattering of individual values of $\langle \Delta E \rangle_{down}$ is, however, much higher in the case of higher barrier, which makes the temperature dependence of $\langle \Delta E \rangle_{down}$ Unimolecular Decomposition of t-C₄H₉ Radical



Figure 8. "Reduced" function $(\langle \Delta E \rangle_{down}$ divided by corresponding T dependence function, as in Figure 6) vs pressure obtained using the modified model of reactions 1 and -1 (see text, section III.5). (a) Values obtained with barrier for decomposition changed by +3.1 kJ mol⁻¹; (b) values obtained with barrier for decomposition changed by -3.1 kJ mol⁻¹.

more uncertain. The "reduced" values of $\langle \Delta E \rangle_{down}$ ($\langle \Delta E \rangle_{down}$ divided by corresponding T dependence function, as described earlier) have no pronounced pressure dependence within the scatter of the data in both cases (Figure 8). The results obtained in the case of the lower barrier, however, display some trend toward negative "pressure dependence".

This variation of the barrier height for decomposition ΔE^{0}_{1} changes the high-pressure limit rate constant k_{1}^{∞} by a factor of 1.86 at 600 K, thus moving it outside the uncertainty limits of the experimental determination by Canosa and Marshall.¹⁵

The cumulative uncertainty in the three important energy parameters of reaction places $\langle \Delta E \rangle_{down}$ between 155 and 387 cm⁻¹ at 750 K. An average value of 230 cm⁻¹ is obtained if the reported values of these parameters are used. This average value is what can be expected based on values for other alkyl radicals which have now been determined.^{9-13,49}

IV. Discussion

1. Temperature Dependence of $\langle \Delta E \rangle_{down}$. This study provides the first set of direct determinations of k_1 in the falloff region and the first opportunity to obtain quantitative information on weakcollision effects in this reaction through master equation analysis using the known thermochemistry of the system and available kinetic information on k_{-1}^{∞} . Values of $\langle \Delta E \rangle_{down}$ were obtained from each experiment in order to obtain an indication not only of the magnitude of this energy-transfer parameter but also of its temperature dependence.

The question of temperature dependence of $\langle \Delta E \rangle_{down}$ has been discussed by many authors (refs 9 and 10 and references therein). Our analysis of the $C_2H_5 \rightleftharpoons H + C_2H_4$ system 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 $\langle \Delta E \rangle_{down}$ = 0.255*T* cm⁻¹. The study of the *i*- $C_3H_7 \rightleftharpoons H + C_3H_6$ system¹⁰ also supports a strong temperature dependence of $\langle \Delta E \rangle_{down}$ for He as bath gas. The modified strong collision/RRKM analysis by Seakins et al.¹⁰ of data obtained at low (298–473 K) and high (750–840 K) temperatures in He as bath gas by several authors yielded values of 13–40 cm⁻¹ at 298 K, 34 cm⁻¹ at 390 K, 40 cm⁻¹ at 473 K, and 136 cm⁻¹ at 750–840 K. The apparent very steep temperature dependence of $\langle \Delta E \rangle_{down}$ for the unimolecular decomposition of the *t*- C_4H_9 radical obtained in the current study is unprecedented and may be caused by uncertainties in the highpressure-limit rate constant and in the thermochemistry of the reaction as described above. The change of the decomposition barrier height by +3.1 kJ mol⁻¹ makes the temperature dependence less steep but results in some discrepancy between the predicted high-pressure-limit rate constant and the values reported by Canosa and Marshall.¹⁵ The change in the barrier height also yields values of $\langle \Delta E \rangle_{down}$ which are probably too high (average of 387 cm⁻¹, compared to 250 cm⁻¹ for C₂H₅,⁹ 220 cm⁻¹ for n-C₃H₇,¹¹ 136–210 cm⁻¹ for *i*-C₃H₇,¹⁰ 140–280 cm⁻¹ for CH₃-CO,¹² 255 cm⁻¹ for CH₃CHCl,¹³ and 300 cm⁻¹ for neo-C₅H₁₁⁴⁹).

For rate constant extrapolation purposes, we employ the model of the system reported here using the known thermochemistry of reactions 1 and -1 which provides k_1 and k_{-1} values in agreement with the current experimental results and those of Canosa and Marshall.¹⁵ We prefer to adopt a directly proportional temperature dependence of $\langle \Delta E \rangle_{down}$:

$$\langle \Delta E \rangle_{\rm down} = 0.309 T \ {\rm cm}^{-1}$$
 (XIV)

based on indications that such dependence is appropriate for other systems, particularly the $C_2H_5 \rightleftharpoons C_2H_4 + H$ system. The significant uncertainty in $\langle \Delta E \rangle_{down}$ makes the apparent temperature dependence unreliable.

The comparison between experimental values of k_1 and those calculated by the master equation/RRKM method using expression XIV for $\langle \Delta E \rangle_{down}$ indicates that deviations between experimental and calculated values are within experimental uncertainty limits (10% in the middle of temperature range and 20% at the extremes), although biased.

2. Thermochemistry of the t-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 tertbutyl radical. This approach was used by Canosa and Marshall,¹⁵ who used their values of $k_1(T)$ and the results of $k_{-1}(T)$ measurements by Canosa et al.¹⁸ Their reported value of $\Delta H_f^{\circ}_{300}$ - $(t-C_4H_9) = 43.9 \pm 4.2$ kJ mol⁻¹ is significantly lower than the recently reported value of Seakins et al.³⁶ ($\Delta H_f^{\circ}_{298}(t-C_4H_9) =$ 51.3 ± 1.8 kJ mol⁻¹) that we used in our model of the transition state of reactions 1 and -1.

Our model with the chosen thermochemistry, however, correctly predicts the magnitudes and the temperature dependences of k_1 and k_{-1} reported by Canosa and Marshall¹⁵ and Canosa et al.¹⁸ (Figure 3). This fact can be explained by comparing values of $\Delta G_{\rm f}^{\circ}(t-C_4H_9)$ at T = 600 K, which can be obtained directly from experimental results of Canosa et al.^{15,18} and Seakins et al.³⁶ The temperature of 600 K was chosen because it lies in convenient proximity to the experimental temperature intervals of all three studies. The experimental data of Canosa et al.^{15,18} and Seakins et al.³⁶ provide the same (within the error limits) value of ΔG_{f}° of the tert-butyl radical at 600 K: $\Delta G_1^{\circ}_{600}(t-C_4H_9) = 237.1 \pm$ 3.2 kJ mol⁻¹ from the results of Canosa et al.;^{15,18} $\Delta G_{\rm f}^{\circ}_{600}(t C_4H_9$ = 237.5 ± 1.5 kJ mol⁻¹ from the results of Seakins et al.³⁶ The difference in the reported values of the enthalpy of formation of the *tert*-butyl radical has its origin in the difference between the $t-C_4H_9$ models used by these authors to calculate the entropy and temperature corrections for enthalpy of the tert-butyl radical.

Taking as a starting point the $\Delta G_r^{\circ}_{600}$ (where "r" in subscript stands for reaction -1) value obtained from the experimental data of Canosa and Marshall and Canosa et al., one can implement two different models of reactions 1 and -1 to elucidate the origin of disagreement in enthalpies. One of the models is that used in the current study (described in section III.2), with the information on the *tert*-butyl radical taken from Pacansky et al.³³ The other model is that used by Canosa and Marshall in their calculations in which the barrier for internal rotation of methyl groups in *tert*-butyl is assumed to be equal to 10.0 kJ mol⁻¹, vibrational frequencies of *tert*-butyl are taken to be 2960(9), 1440(9), 1300(2), 990(6), 710(1), 480(2), and 250(1) cm⁻¹, and the thermodynamic information on isobutene is taken from ref 50.

From these data the authors^{15,18} calculate $\Delta S_{r,600} = -115.4$ J mol⁻¹ K⁻¹ at 1 atm⁻¹, while $\Delta S_{f}^{\circ}_{600}$ calculated using the model used in the current study is equal to -108.7 J mol⁻¹ K⁻¹. Therefore, the difference in values of $\Delta H_r^{\circ}_{600}$ calculated by subtraction of $-T\Delta S_{r,600}$ from $\Delta G_r^{\circ}_{600}$ for these two models is 4.1 kJ mol⁻¹. The $(\Delta H_r^{\circ}_{600} - \Delta H_r^{\circ}_{298})$ values, calculated using the two models mentioned above, supplies another 2.4 kJ mol⁻¹ of difference between the values of the enthalpy of formation of the $t-C_4H_9$ radical.

After the differences in the models are taken into account, the experimental data by Canosa et al.^{15,18} lead to $\Delta H_f^{\circ}_{298} = 50.8$ kJ mol⁻¹, which is 0.5 kJ mol⁻¹ smaller than the result of Seakins et al.³⁶ This difference coincides with the difference between the values of ΔG_{f}° of the tert-butyl radical at 600 K from the results of Canosa et al.^{15,18} and from the results of Seakins et al.³⁶

Tsang⁶ calculated the heat of formation of the tert-butyl radical using the results of Harris and Pitts¹⁷ on the k_{-1} temperature dependence and those of Birrell and Trotman-Dickenson¹⁶ and Canosa and Marshall¹⁵ on $k_1(T)$ values. He obtained two values: $\Delta H_f^{\circ}_{298} = 51.7 \pm 2.2 \text{ kJ mol}^{-1}$ if methyl rotors in t-C₄H₉ are free, and $\Delta H_{\rm f}^{\circ}_{298} = 46.2 \pm 2.2 \,\rm kJ \, mol^{-1}$ if 10 kJ mol⁻¹ barriers for CH₃ rotors are assumed. If the 6.3 kJ mol⁻¹ value³⁴ (used in our model) for these barriers is assumed, one would expect $\Delta H_{\rm f}^{\circ}_{298}(t-{\rm C_4H_9})$ to be close to the average of these two values. The higher $\Delta H_{f}^{\circ}_{298}(t-C_{4}H_{9}) = 51.3 \text{ kJ mol}^{-1}$ value of Seakins et al. used in our model results in a somewhat higher activation energy and rate constants of reaction 1 (section III.2). This reflects the fact that Tsang used the results of Birrell and Trotman-Dickenson along with those of Canosa and Marshall to characterize the k_1 temperature dependence, while we considered the results of Birrell and Trotman-Dickenson not to be useful for reasons discussed in section III.2.

V. Parametrization of Rate Constants

We present here a parametrization of k_1 in helium and nitrogen which provides the 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.⁵¹ was used:

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

Values of $k_1(M,T)$ in the above temperature and pressure intervals were calculated using the master equation/RRKM approach assuming the directly proportional temperature dependence of $\langle \Delta E \rangle_{down}$ (XIV) for helium as the bath gas. Analogous calculations were done for nitrogen as the bath gas. Since no experimental measurements are available for nitrogen, we presumed that the $\langle \Delta E \rangle_{\text{down}}$ value for nitrogen at 750 K is approximately equal to that for helium (XIV). This presumption is based on the results of earlier studies of the unimolecular decomposition of n-C₃H₇¹¹ and i-C₃H₇.¹⁰

The matrix of calculated values of $k_1(M,T)$ was fitted with the modified Lindemann-Hinshelwood expression XV, and the resulting parameters are

$$k_1^{\infty} = 2.18 \times 10^9 T^{1.48} \exp(-18120 \text{ K}/T) \text{ s}^{-1}$$

and

$$k_1^0 = 2.29 \times 10^{33} T^{-12.0} \times \exp(-21290 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}$$

$$F_{\text{cent}} = 0.344 \exp(-T/1158 \text{ K}) + 9.45 \exp(-6857 \text{ K}/T)$$

for helium as bath gas

$$k_1^0 = 1.12 \times 10^{33} T^{-12.0} \times$$

 $\exp(-21220 \text{ K/T}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
 $F_{\text{cent}} = 0.355 \exp(-T/1431 \text{ K}) + 15.85 \exp(-7220 \text{ K/T})$

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 40%.

Due to the uncertainty in the temperature dependence of $\langle \Delta E \rangle_{\rm down}$ discussed above, 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 $t-C_4H_9$ in helium has been studied in the falloff region. A transition-state model of reaction 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. A convenient formalism for the treatment of internal hindered rotors was introduced which provides simple formulas for the density-of-states and sum-ofstates functions.

The experimental values of k_1 were reproduced by master equation/RRKM modeling, and the temperature dependence of $\langle \Delta E \rangle_{\rm down}$ was addressed. Finally, parametrized expressions are presented which provide values of k_1 over a wide range of pressures and temperatures.

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